ADSORPTION ON ACTIVATED CARBON OF HYDROGEN, METHANE AND CARBON DIOXIDE GASES AND THEIR MIXTURES AT 212 K TO 301 K AND UP TO THIRTY-FIVE ATMOSPHERES

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Approved:

Chairman

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DEDICATION

To all those who helped.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

NOMENCLATURE

b	Constant in the van der Waals equation or the Langmuir equation
B	Constant in the Dubinin-Radushkevich equation
BET	Brunauer-Emmett-Teller
BWG	Birmingham wire gauge
BWR	Benedict-Webb-Rubin
cc	Cubic centimeter
cm	Centimeter
D	Data deviation in per cent
EMF	Electromotive force
f	Fugacity
F	Mathematical function
h	Peak height from gas chromatograph analysis
i, j	Integers
k, k_i	An arbitrary mathematical constant
K	Kelvin
ln	Natural logarithm
N	Moles of adsorbate
N^o	Moles of adsorbate from a pure gas phase
N^*	Moles of adsorbate with one monolayer on the adsorbent
P	Total system pressure in absolute units
Pg	Pressure used with the Grant-Manes method defined by equation (IV-12)
P_i	Component partial pressure
Ps	Component vapor pressure

NOMENCLATURE (Continued)

P^o	Pressure from the pure component isotherm
R	Gas constant 0.08206 liter-atm/gm-mole-K
s	Gas chromatograph sensitivity switch setting
T	Absolute temperature
V	Volume of system
$\bar{V}$	Component molar volume
W, Wo	Variables in the Dubinin-Radushkevich equation which represent adsorbate volume
X	Mole fraction in the adsorbate
Y	Mole fraction in the gas phase
Z	Compressibility factor

SUPERSCRIPTS:

A	Adsorbate
L	Liquid
G	Gas

SUBSCRIPTS:

c	Critical
D	Carbon dioxide
G	Grant-Manes
H	Hydrogen
M	Methane
mx	Mixture
P	Partial
R	Reduced property
s	Saturated
T	Total

NOMENCLATURE (Concluded)

GREEK LETTERS:

α	Relative volatility or selectivity defined in equation (V-2)
β	Affinity coefficient in the Dubinin-Radushkevich equation
γ	Analytical accuracy
ϵ	Polanyi Adsorption Potential
Δ	Incremental quantity
μ	Chemical potential
Σ	Summation
σ	Criteria used to check deviation between experimental and calculated quantities
ϕ_A	Adsorption enhancement factor defined in equation (V-5)

SUMMARY

The purpose for this study was to learn the relation which exists between adsorption from multi-component gas solutions at pressures exceeding one atmosphere and the amount of the same material adsorbed from a pure gas phase. It was also desired to study the effect of pressure and temperature changes on adsorption isotherms. Hydrogen, methane and carbon dioxide were chosen as gases with distinctly different molecular properties. These three substances have critical temperatures separated by more than 100 Kelvin degrees. Carbon dioxide and hydrogen are linear molecules and methane is approximately spherical. The adsorbent chosen was activated carbon, Pittsburgh BPL. This material is made from coal and has been available for many years. It is microporous, has a heterogeneous surface and a high adsorption capacity. It has been used by others[7, 15, 21] in adsorption studies.

Adsorption was determined at three temperatures; 212.7, 260.2, and 301.4 K. All of the experiments were below the critical temperature of carbon dioxide and above those for methane and hydrogen. The ternary mixtures were tested to 35 atmospheres. Binary mixtures containing the same approximate molar ratios of methane and carbon dioxide as the ternaries were run to six atmospheres which exceeds the partial pressure of these components in all of the ternaries. Pure gas isotherms were determined for the components at each temperature level to seven atmospheres except that the lowest temperature carbon dioxide isotherm was limited to three atmospheres.

The compositions of the binary mixtures in mole per cent were 18.8 methane with 81.2 carbon dioxide, 49.8 methane with 50.2 carbon dioxide, and 79.5 methane with 20.5 carbon dioxide. The ternary mixtures all contained hydrogen as the major component with 2.08 mole per cent methane and 9.77 carbon dioxide, 6.60 methane and 6.95 carbon dioxide, and 10.8 methane with 2.86 carbon dioxide. The amount of hydrogen adsorbed was found to be below the detection limits for the apparatus. All adsorbates from ternary mixtures are reported as binary solutions.

An apparatus was designed and constructed for the determination of the isotherms. Volumetric methods were used to obtain all experimental results.

The pure isotherm data for carbon dioxide and methane were fitted to smooth functions using a least-squares procedure. Of the many types of functions tried, the two-parameter Dubinin-Radushkevich[13] form gave the best results for all of the independent sets of experimental data. No fitting was done for the mixture isotherms as the number of points obtained was not sufficient to make a fitting process meaningful.

Several mixture adsorption models were used with the experimental results from this study. The Langmuir mixture isotherm could not be satisfactorily fitted. The relative volatility and adsorption enhancement factor concepts had very limited utility. The Dubinin-Radushkevich equation as used for mixtures by Bering et al.,[5] was found unsatisfactory. The constants with this equation were temperature dependent in certain cases and the method for predicting adsorbate composition gave significant errors.

Using the Adsorption Potential Theory, a modification of a

concept originally formalized by Polanyi[34], a characteristic curve was constructed which included the adsorption isotherms for pure methane and carbon dioxide at three temperatures and for pressures to 100 PSIA. A characteristic curve based on the mixture adsorption data was shown to be essentially the same as that for the pure components. This agreement shows the general utility of the adsorption prediction method proposed by Grant and Manes[21] for mixtures. Several empirical models for the adsorbate molar volume used in characteristic curve construction have been employed. The recommended procedure is that which assumes that the adsorbate mixture volume can be computed from the molar volumes of the pure saturated liquids at their normal boiling points.

The Grant-Manes[21] method is recommended for the prediction of mixture isotherms when no experimental data for such isotherms are available. For pressures in excess of 100 PSIA where the prediction results are less accurate, an indication of the components which are over predicted or under predicted is given.

CHAPTER I

INTRODUCTION

Adsorption must be considered as a phase equilibrium phenomenon. It occurs when a solid phase is present with a fluid and consists of a greater density or concentration of components from the fluid phase on the solid surface. When the fluid contains more than one species, there is a concentration increase at the solid surface for at least one of the components. The material on the solid surface which is at a greater density than the free bulk phase is called the adsorbate and the solid is called the adsorbent. Depending upon pressure, temperature and species, the adsorbate may exist as a solid, liquid or compressed gas. As the temperature is decreased for an adsorption system in equilibrium with a gas phase at constant pressure, the amount of adsorbate per unit quantity of adsorbent will increase and the adsorbate will pass through phase transitions. However, even when the adsorbate is a pure material, the phase transitions do not occur at the same temperatures as with the non-adsorbed material.

The above description is for the process known as physical adsorption. Another process called chemisorption includes the adsorbate undergoing a chemical reaction with the adsorbent. In physical adsorption, the adsorbent remains chemically inert at all times. The evidence for chemisorption may be direct or indirect. It may be obvious as when new compounds are found in the desorbed material. The molecular bonding between adsorbate and adsorbent is much stronger for chemisorbed

materials. This is evident from the larger quantities of heat release observed on formation of the system and the more severe conditions required to separate the components. It is not always a simple matter to distinguish between physical and chemical adsorption. Over the years, physical adsorption, chemisorption and ion exchange were considered separate topics. Recently, the many points of similarity have led to all of these being included in the category known as sorption processes.

Investigation and measurements of physical adsorption were begun over a century ago. These studies often involved charcoal as this adsorbent has a high capacity for many gases. Measurements were made with the common gases on many different kinds of charcoal. However, the phenomenological approach of classical thermodynamics failed to yield a general understanding of the detailed mechanism of the adsorption process. During the early part of the present century, adsorption was felt to be caused by some special force.

It was not until the work of London in 1930 that beliefs shifted toward the realization that adsorption is the result of normal intermolecular forces. The same intermolecular forces which cause adsorption govern density and phase relations for pure materials. Thus a quantitative description of an adsorption process contributes directly to a better understanding of intermolecular forces for the species involved.

To derive information on a molecular scale, the methods of statistical mechanics are required. To apply statistical mechanics, it is necessary to study systems which can be defined with mathematical precision. Simple molecular shapes for adsorbates and well-defined

homogeneous adsorbents must comprise the systems for study of the elementary adsorption process. After these simple systems are fully understood, attention can be turned to more complex systems involving heterogeneous adsorbents.

Applications of physical adsorption in complex systems were in commercial use long before the nature of the forces involved was recognized. Adsorption is a practical process for the removal of trace amounts of components from mixtures. It has proven useful for the elimination of color bodies from liquids and odors from gases. It is used extensively to remove water vapor, carbon dioxide, acetylene, and methane from air for the air separation process. There are a number of generic types of adsorbents commercially available for gas processing. These include:

1) Activated carbon.

2) Silica gel.

3) Molecular sieves or zeolites.

4) Alumina.

Of this group, activated carbon is known as a non-polar adsorbent as it does not show preferential adsorption for polar molecules. The type and degree of bonding varies with each adsorbent and the conditions required for adsorbate removal will differ. Regeneration is an important consideration in the commercial application of adsorption. The possible steps used for desorption include:

1) Heating the system.

2) Evacuating the system.

3) Purging the adsorbent with a gas free of the adsorbate material.

All commercial applications of adsorption are involved with the separation of components from fluid mixtures. Much of the data and most of the design methods for commercial adsorption systems have been developed empirically. The scientific literature contains much on the adsorption of pure components on many different adsorbents. The desired goal for engineering purposes is to develop methods to allow pure component isotherm data to be used for the prediction of equilibrium adsorption effects from mixtures. It is necessary that these techniques allow the prediction of amounts which will be adsorbed at any given set of pressure-temperature conditions for a specified adsorbent.

Available Experimental Methods

Since the isotherm gives the relation between pressure and the amount adsorbed with adsorbent and adsorbate at constant temperature, it is apparent that the apparatus must maintain the system at a fixed temperature. Two techniques are available for the experimental determination of pure gas isotherms.

The gravimetric technique weighs the adsorbent which is freely suspended in the gas phase. A buoyancy correction is required to give the accuracy necessary for determination of the amount of adsorbate on the solid. The gravimetric technique avoids the need for determination of system volumes other than that of the adsorbent.

The volumetric method is based on an exact material balance knowing the amount of gas admitted to the system and the amount remaining in the gas phase. It is necessary to know the pressure, temperature, gas deviation from ideal behavior, and system volumes. The basic relation for determining adsorption by the volumetric technique is

(Gas adsorbed) = (Gas admitted to System) -

(Gas in System Dead Space) (I-1)

The "dead space" is the calibrated gas phase volume within the adsorption system. It may also be considered as the total volume within the system less the volume occupied by the adsorbent. For a pure gas isotherm, a series of experimental values are obtained by starting with the adsorbent system fully evacuated and then allowing a known amount of pure gas to enter the system from a calibrated reservoir. After the pressure within the system reaches equilibrium, the value is recorded and additional doses of gas may be admitted to obtain a series of points relating pressure to the amount adsorbed. Complete information is available on the amount of gas in the dead space and adsorbed phases at each stage of the determination. The volumetric method was used in this investigation for pure gases and mixtures.

The calculation using equation (I-1) results in a Gibbs adsorption value. There is no correction made for the volume occupied by the adsorbate. The calculation based on using a dead space volume less the volume occupied by the adsorbate gives a result known as total adsorption. Total adsorption values are always higher than Gibbs adsorption results. The difference is not significant with the volumetric method until the component pressure is high. It should be noted that with the gravimetric method, allowing for the adsorbate volume increases the buoyancy correction.

The problem of experimentally determining adsorption from mixtures is more difficult since the adsorbate composition is an unknown. With the volumetric method, it is not possible to obtain a series of

pressure and amount adsorbed values during a single experimental run. Two different volumetric mixture methods are available. The first involves charging a known amount of a gas mixture of known composition into the fully evacuated adsorption system. The gas is circulated through the adsorbent until pressure equilibrium is reached while maintaining isothermal conditions. After equilibrium, a sample of the gas phase is removed and analyzed without changing the pressure on the adsorbent. The gas analysis together with a knowledge of the pressure, temperature and dead space volume, and knowing the deviation from ideal gas behavior, allows the calculation of the amount of each component adsorbed.

Another possibility for mixture isotherm determination, the method used in this study, is to continuously flow the known gas mixture through the adsorbent at constant pressure and temperature until the effluent gas from the adsorbent has the same composition as the feed gas. After equilibrium has been reached, all gas and adsorbate is removed from the closed system and the amount is measured and the total removed gas is analyzed. These results together with the knowledge of the amount and composition of mixture that was in the dead space are sufficient to calculate the amount of each component which was adsorbed at the experimental temperature and pressure.

The exact procedures used in this investigation for determination of pure gas and mixture isotherms are given in Appendix D. A detailed description of the apparatus is given in Chapter II and Appendix A.

Activated Carbon Adsorbent

Specification of an adsorbent, particularly heterogeneous materials, is usually more inaccurate than the description for the adsorbate and gas phases. Chemical composition of the adsorbent is only one item of many needed for a rigorous description. The nature of the surface is a most important factor. A quantitative indication of the pore sizes can be as important as the amount of apparent surface area when trying to anticipate the action of an adsorbent in a given application. In commercial practice, manufacturers give their adsorbents type designations and then produce them by established methods to produce a consistent product.

The adsorbent chosen for this study is a microporous activated carbon with a heterogeneous surface which has been available commercially for several years. It is Pittsburgh type BPL which is made from coal. A heterogeneous adsorbent was chosen for this study as this group is of the greatest importance in mixture separation. The particular type was chosen as it seemed fairly typical of the several activated carbons available and several studies by others employed the same material[7, 15, 21].

As a part of the investigation, a conventional nitrogen BET surface determination and mercury porosimeter test were performed on a portion of the carbon from the same batch as that used in the apparatus. Results of these tests and manufacturer's data for the material are reported in Table 1.

Table 1. Carbon Adsorbent Characteristics

Manufacturer: Pittsburgh Activated Carbon Division, Calgon Corp.

Manufacturers Type BPL

Mesh Size 20/60

Data from Manufacturer:		
	Bulk Density	0.5 gm/cc
	Particle Density	0.8 gm/cc
	Real Density	2.1 gm/cc
	Pore Volume	0.8 cc/gm

Micropore size by water desorption isotherm shows major portion in the 18 to 20 Angstrom diameter range.

Data determined in this study:

1) Total Surface Area by Nitrogen BET Method was 967 Square Meters/gm.
2) Mercury porosimeter test showed pores beginning at 2 micrometers and extending fairly uniformly to smaller diameters to the limit of detectability for this test which is 35 Angstrom units.

The carbon was crushed and sieved prior to loading in the adsorbent vessel. The amount of carbon put in the apparatus was 35.38 grams. Many preliminary isotherms for the three pure gases used were run before the actual record data was obtained. A series of regeneration experiments was also run as reported in Chapter II to verify that the desorption technique was satisfactory.

The BET surface measurement performed for this study indicated a

surface area between the value found by Cook[7] and that reported by the manufacturer for the same adsorbent. Based on the BET surface area determination and the favorable comparison of the pure methane and carbon dioxide isotherms with the published results of others as discussed in Chapter III, it was believed that the carbon used for this study was a typical sample.

Scope of This Work

The purpose of this investigation was to study physical adsorption from gas mixtures. It was to learn if the amount adsorbed from binary and tenary mixtures could be related to the pure component isotherms. It was also hoped that relations could be found to predict the effects of pressure and temperature changes on the adsorption isotherm.

The three gas components chosen were hydrogen, methane, and carbon dioxide. These materials have distinctly different molecular properties. Their critical temperatures differ by over one hundred Kelvin degrees. The highly adsorbed components are methane and carbon dioxide. Methane is an approximately spherical molecule; hydrogen and carbon dioxide are linear molecules.

The pressure limit chosen for the ternaries was 35 atmospheres. This was felt to be adequate to test prediction theories and cover the range of common engineering interest. The binary mixtures were determined to six atmospheres which fully duplicated the partial pressure range for the components in the ternaries. The pure isotherms were run to seven atmospheres.

Three temperatures were used for the experiments to determine the effect of temperature on adsorption. The three temperatures were 212.7,

260.2, and 301.4 K.

The three binary mixtures used had the composition (in mole per cent) 18.8 methane and 81.2 carbon dioxide; 49.8 methane and 50.2 carbon dioxide; 79.5 methane with 20.5 carbon dioxide.

In the ternary mixtures, hydrogen was the major component and the methane and carbon dioxide were present in approximately the same molar ratio as for the binaries studied. The ternary compositions were 2.075 mole per cent methane and 9.77 carbon dioxide; 6.60 methane and 6.95 carbon dioxide; 10.8 methane and 2.86 carbon dioxide. Hydrogen was the remainder for all the ternary mixtures above.

There are no data reported in the literature for the binary or ternary systems covered in this study. Some isotherms for pure methane and carbon dioxide on the same or similar adsorbents have been reported[18, 21, 22]. No other investigation to date has covered the same scope of adsorption determinations with the same adsorbent sample. All experimental results are reported in Appendix E and discussed in Chapter III.

Prediction Models

Various theoretical and empirical methods have been proposed for the prediction of adsorption from gas mixtures. Of these the empirical models offered the greater hope for success because of the heterogeneous adsorbent used for this study. Because prediction for the ternary mixture was a primary purpose for this study, methods limited to binary systems were not considered. Of the two highly adsorbed components in in this study, methane was above and carbon dioxide was below its critical temperature for all of the isotherms.

The mixture prediction method which has been shown to give good results at pressures above atmospheric and with at least one of the gas phase components above the critical temperature is the modified Polanyi Potential Theory as applied by Grant and Manes[21]. The Polanyi approach has generally proven successful with heterogeneous adsorbents where other methods have failed. A different modification of the Polanyi theory has been applied by Bering et al.[5] to binary mixtures below the critical temperature for both components at pressures below one atmosphere. This method uses the Dubinin-Radushkevich equation. The method is not limited to binaries. These theories, methods, and results are discussed in detail in Chapters IV and V.

A modification of the Grant-Manes[21] adsorption prediction method was found to be the most successful of the various approaches studied. Details of this method and a graphical comparison with the experimental findings of this investigation are presented in Chapter V.

CHAPTER II

EXPERIMENTAL APPARATUS

It was necessary to design and construct an apparatus to obtain the data desired for this study. Since it was anticipated that other adsorption problems would be studied on the same equipment, the design was done with a view toward flexibility. The adsorption system was designed for operation to 100 atmospheres. The cryostat system is capable of operating in the temperature range from 70 to 350 K.

Several techniques have been described and proven successful for the determination of adsorption data[6, 7, 15, 42]. The design choices for this study favored the mechanical features appropriate for the fabricating capability available and also the system judged to give the desired test conditions with the greatest operating stability.

A volumetric method was used for both the pure gases and the mixtures. A static equilibrium technique was used for pure gases. An open system flowing method was used for mixtures. The same piece of equipment with necessary modification was used for the two different systems. The same adsorbent sample (35.38 gms) was used for all experiments (see Table 1, Chapter 1).

A schematic diagram of the pure isotherm apparatus is shown as Figure 1. The adsorbent cell is located within the cryostat. Either water or hexane were used as the cryostat fluid depending upon the temperature for the experiment. A schematic diagram of the system within the cryostat is shown in Figure 24 and this with a detailed description

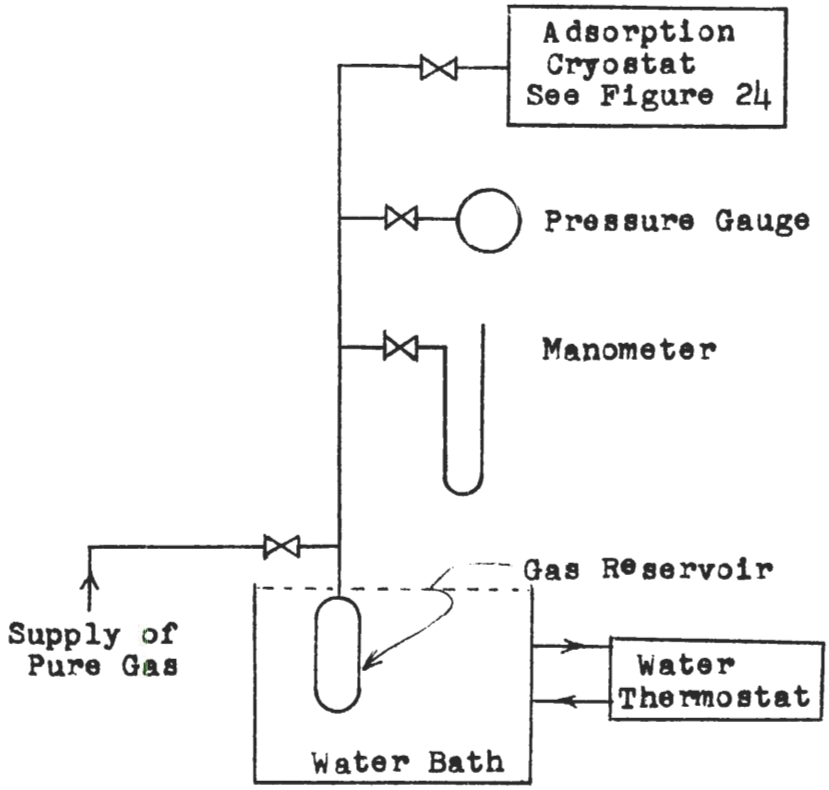

Figure 1. Schematic Pure Isotherm System

is in Appendix A. The pure gas was in a calibrated reservoir submerged in a separate water thermostat. The pressure and temperature devices are discussed in detail in a later part of this chapter and in Appendix A. Thermocouple calibration is covered in Appendix B.

For mixtures, the once-through flow technique described in Chapter I was used. This choice was dictated by the fact that the circulating technique allows no control over the final pressure or gas phase composition.

Sub-systems were added to the pure isotherm apparatus to make it suitable for the determination of mixture isotherm points by the flow technique. A gas-dome type pressure regulator was used to control the feed gas pressure into the unit from a commercial steel gas cylinder. A heat exchanger brought the feed gas close to the temperature of the effluent gas from the adsorbent. A coil within the cryostat brought the gas to the desired temperature before it entered the adsorbent vessel. From the heat exchanger, the effluent gas went either through a positive displacement meter or the gas analysis unit. For the desorption part of the experiment, the cryostat was removed and heaters attached to the adsorbent vessel. The desorbed gas flowed to a calibrated sample reservoir located in the water thermostat. In the same thermostat was the gas reservoir used for the pure isotherms. For mixture isotherms, this reservoir contained pure hydrogen sweep gas to purge the adsorbent and all system tubing to insure that all adsorbate had been moved to the sample reservoir. The sample reservoir had a mixer driven by a magneticly coupled motor. The schematic diagram for the mixture isotherm system is shown as Figure 2. The analysis of mixtures was accomplished

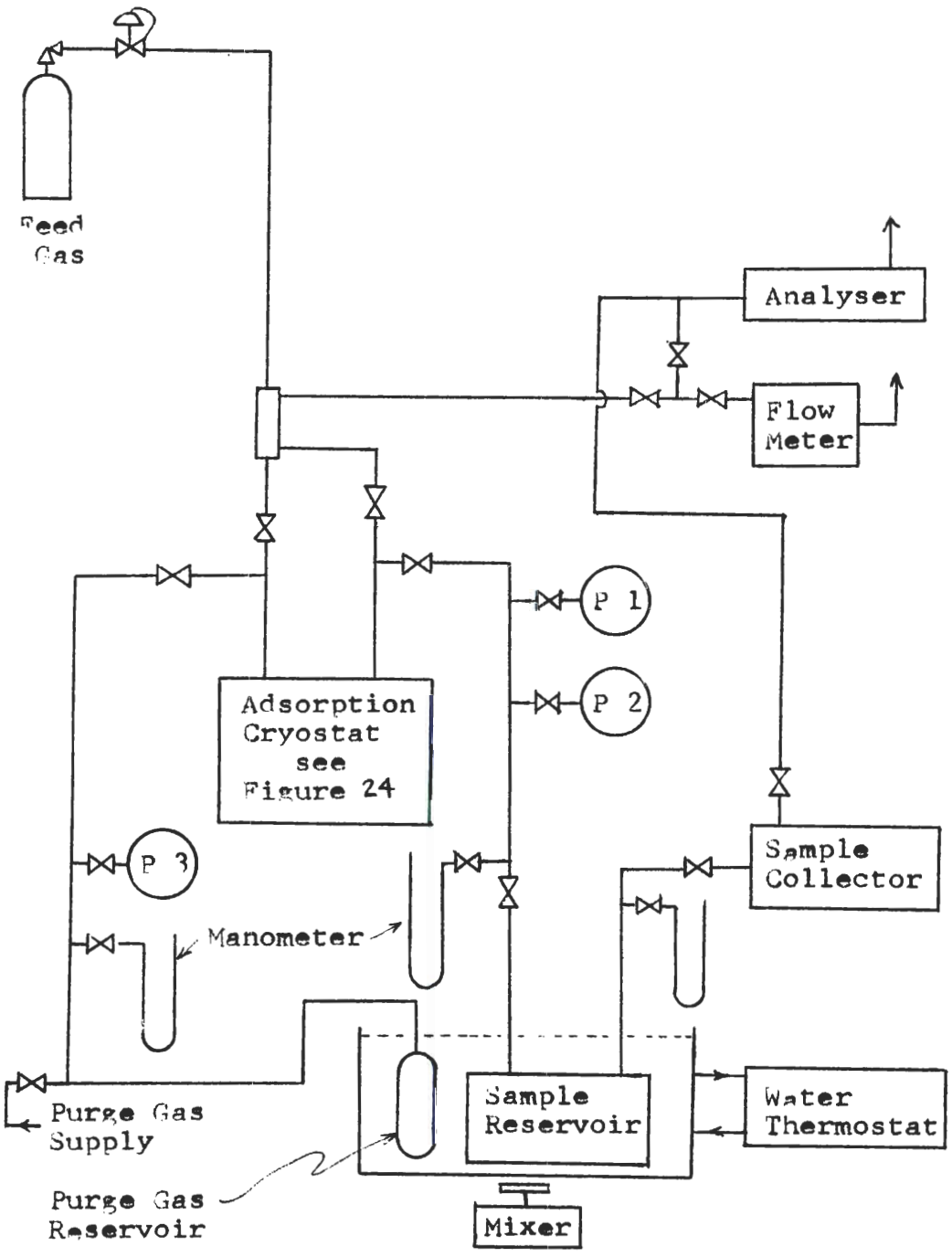

Figure 2. Schematic Mixture Adsorption System

with a gas chromatograph. Details of this instrument and calibration information are given in Appendix C. Gas mixture preparation is discussed in Appendix F.

Pressure Measurements

Pressure was measured by either mercury-in-glass manometers for pressures below two atmospheres or Bourdon type gauges for higher levels. Vacuum below the detection limits of the manometers was checked with a Bendix Type GTC-100 thermocouple type vacuum gauge. This instrument had two detectors. One was installed in the vacuum manifold and the other to the adsorbent cell system. This instrument was checked before and several times during the several month period when experiments were being run by using a McLeod gauge. It was always found to be satisfactory. The manometers were all checked in place with a cathetometer and a standard meter bar, Serial 151AU, from Gaertner Scientific.

The pressure gauges were all calibrated by the use of an Ashcroft Portable Dead Weight Tester manufactured by Manning, Maxwell and Moore, Type 1305B-100, Serial 55545. The tester was in new condition and the manufacturer certified the accuracy to 1/10 per cent of indicated values. Pressure gauges from three different manufacturers were tested. The agreement of the calibration results with the claimed accuracy of the gauge manufacturers was accepted as indirect confirmation that the dead weight tester had no serious faults.

The internal volumes of the pressure gauges and the manometers were determined by helium displacement measurements made before the adsorption experiments began. The particular unit which was included in the system during an experimental step and all measured values

were recorded on punched cards for input to the computer program used to calculate the isotherms. The mercury manometer internal volume was known as a linear function of pressure and this computation was made within the program. The internal volumes for the pressure gauges were found to be independent of the pressure over the range in which they were used and within the accuracy of the volume determinations.

For medium pressure in the adsorption dead space, an Ashcroft 8 inch Model 1850, 0 to 300 PSIG test gauge P-1, was used. The gauge was purchased new for the apparatus. It was checked with the dead weight tester and found to be within the manufacturers claim of 1/4 per cent of range accuracy. The correction plot for this gauge is presented as Figure 25 in Appendix A.

High pressure gauge, P-2, used for the dead space, had been employed previously on a dew-point apparatus constructed by McCain[30]. It is a Martin Decker Model GB-10-150, Serial 1175, 0 to 1,500 PSIG 8 inch gauge. This gauge was calibrated to 1,450 PSIG. The correction required to make it agree with the dead weight tester was plotted as a function of pressure with error bars to allow for readability and accuracy. This correction plot is presented as Figure 26 in Appendix A. All pressure gauge readings were corrected before use as input to computer programs.

Pressure gauge P-3, used on the reservoir for gases during the pure isotherm measurements and for hydrogen purge gas during the mixture experiments, is a Heise Model CM-8457, 6", 0 to 250 PSIG unit with a claimed accuracy of 1/10 per cent. This claim was confirmed for the range above 15 PSIG where the gauge was used. This gauge was purchased

for this project. Since this gauge was found accurate to the limits of readability, no correction plot was required.

Temperature Measurement and Control

Precision mercury-in-glass thermometers were used to read the room and water thermostat temperatures. The calibration of these thermometers was checked when the thermocouples were calibrated. A mercury thermal switch controlled the water thermostat heaters. All temperatures in the cryostat were read and controlled by thermocouples.

The low temperatures for the present study and future work anticipated in the cryogenic region led to the choice of Type E, Chromel-Constantan thermocouples following the recommendation of Sparks et al.[38]. Two of these thermocouples were installed in separate glass wells in the cryostat and these two were calibrated by using a platinum resistance thermometer as a reference standard. Details of the calibration are presented in Appendix B. All thermocouples on the unit used a common water-ice reference bath.

The calibrated thermocouples were read with a potentiometer circuit which included a standard cell made by Eppley Laboratories, No. 233715, and the following components manufactured by Leeds and Northrup:

D. C. Null Detector, Catalogue No. 9834

Standard resistor, 10 Ohm, No. 624178

K-3 Universal Pontentiometer, Catalogue No. 7553-5.

The two calibrated thermocouples were located within 10 cm of the adsorption cell. A third bare thermocouple made from the same Chromel and Constantan wire was installed in the cryostat and used to record temperature during each isotherm experiment on a strip chart millivolt

recorder.

A double junction thermocouple was made from the same wire and installed bare in the cryostat for the purpose of controlling the temperature. This control thermocouple was installed in series with a galvanometer and a Model 8662 potentiometer, both manufactured by Leeds and Northrup. The galvanometer was the type which reflected a light onto a frosted glass. When the galvanometer went up-scale, it actuated a photocell relay circuit which controlled either an electric heater installed in the cryostat or a solenoid valve which controlled the flow of liquid nitrogen through the cryostat cooling coil. The potentiometer supplied an opposing EMF and the system could be set to balance at any desired temperature. A second photocell on the galvanometer with a holding relay kept the system from reacting when the light went too far up-scale. The system was manually connected, to heat or cool only, before each experimental run. This temperature control system maintained the adsorption cell cryostat within 0.1 Kelvin degree of the set temperature.

The original adsorption vessel installed on the apparatus was different from the one described in Appendix A and used in the experiments for the reported adsorption data. The original vessel contained five grams of carbon and included a bare thermocouple within the cell in close proximity to the adsorbent at the effluent end. Many pure and a few mixture isotherm points were determined with the original cell. The internal thermocouple proved useful because it verified that there were no unusual temperature fluctuations near the adsorbent during any part of the experimental runs. This internal thermocouple was also used to verify that the surface temperature of the vessel was a satisfactory

guide to indicate when the adsorbent had reached the temperature required for desorption. The original adsorption cell was replaced by a larger vessel when an error analysis indicated that the larger than anticipated apparatus dead space volume was causing insufficient precision in the adsorption measurements for methane at 301.4 K.

Adsorbent Regeneration

Removal of adsorbate from the carbon was vital in these experiments. For the pure isotherms, it was necessary to be certain that essentially no adsorbate was present before beginning each determination as this would result in a reduced indicated capacity. In the case of the mixture experiments, removal and collection of all adsorbate at the end of the contact period was necessary to determine the amount of each adsorbed component.

For the pure isotherms, the steps chosen for regeneration were heating and evacuation. A series of experiments was run for pure carbon dioxide and methane isotherms to determine the minimum conditions required for regeneration. Minimum conditions are defined for this study as those which suffice to give a subsequent isotherm determination with no apparent decrease in adsorbent capacity. Temperatures to 465 K and evacuation times to twelve hours were used initially. The vacuum system was found to be capable of a vacuum of 20 to 40 milli-Torr when operating on the vacuum manifold only. This series of tests showed that three hours evacuation at room temperature was sufficient to restore the carbon to the same condition as was achieved with the maximum evacuation time and temperature used for both the carbon dioxide and methane isotherms. In the case of the methane, it was found that less

evacuation time was required. This was thought to be due to the fact that less was adsorbed at the end of a methane determination and the activation energy required to desorb methane is less.

For adsorbate desorption as a part of the mixture experiments, the operations employed were heating and purging. A comparable series of experiments to those described above was run beginning with mixed adsorbate on the carbon. The variables in this case were the temperature to which adsorbent was heated and the amount of hydrogen purge gas. It was found that heating the adsorbent to 360 K and sweeping with at least 200 cc of hydrogen at room temperature and pressure was sufficient to remove the methane and carbon dioxide to a level which would not affect the subsequent experimental results. In practice, the adsorbent was also reduced to a pressure below atmospheric when the adsorbent system was connected to the evacuated sample reservoir as the last sample was collected. The pressure on the adsorbent was 2 PSIA or less for the final sample during all mixture experiments.

To be certain there were no cumulative effects on the adsorbent, certain of the pure and mixture isotherms were repeated after an interval of at least a month with many experiments run in between these tests. These tests showed no decrease in adsorption capacity. These runs are identified in Tables 5, 7 and 11 which are in Appendix E.

CHAPTER III

EXPERIMENTAL RESULTS

The two different experimental isotherm methods used for the data obtained for this study have been described in a general manner in the two previous chapters. The detailed experimental procedures for pure and mixture isotherms are given in Appendix D.

All isotherm values were calculated with Fortran programs on a Univac 1108 computer. The basis for the calculation is a detailed material balance. In these calculations, the correction for non-ideality of the gas phase was significant for the higher pressures and the two lower temperatures. This correction was computed from a BWR equation in a program sub-routine. The correction was made for all points. The BWR constants and mixture rules employed were those given by Orye[32].

All of the experimental work performed was for the purpose of obtaining equilibrium data. Brunauer[6] indicates that the attainment of equilibrium is usually very rapid where chemisorption is not present. The pure isotherms in this work were all repeated at various times to check reproducibility. With the smaller adsorption vessel described in Chapter II, a desorption point was obtained as a part of each pure isotherm experiment. The technique used when this smaller vessel was on the apparatus involved opening a valve when changing from a manometer to a pressure gauge to determine the system pressure. When the valve was opened connecting the evacuated pressure gauge to the system, there was a decrease in the system pressure, and recording the readings after

stability was attained (approximately one minute) gave a desorption point. There were several determinations each for methane and carbon dioxide. It was found that the desorption points fell on the fitted isotherms for all cases. This showed lack of hysteresis. It also gave a confirmation of equilibrium with the technique employed for these components in the apparatus.

Checks were made to verify that kinetic effects were not present with the methods and rates used. In the determination of the pure isotherms, the worst error from kinetic effects would be if insufficient time were allowed before recording the pressure. A number of experiments were run in which the time between readings was increased by a factor of three. There were no differences in the resulting isotherms. For the mixtures, too high a flow rate could result in an effluent gas that was not in equilibrium with the adsorbate. To verify that such an effect was not occurring with the rates used, the feed gas rate was reduced in several experiments, after the system seemed to be in equilibrium. The rate was reduced to half and then one fifth of the normal flow rate. No change was observed in the effluent gas composition with the reduced rate. It should also be noted that in every mixture experiment, after equilibrium is indicated by the effluent gas composition being equal to the feed gas, there is additional contact time while one to three more check analyses are made of the feed and effluent gases. Each analysis requires seven minutes.

An attempt at error analysis was made for all of the kinds of data obtained and reported. This subject is discussed in detail in Appendix G. The possible error for a particular point depends upon the

magnitude of the measured variables. As a reasonable approximation, it is thought that the pure isotherms for methane and carbon dioxide may be considered to have a precision of 5 per cent. For the mixtures, the errors due to analysis and multiple samples must be added to the basic system errors. As a general approximation, it is felt that the methane adsorption values reported for binary and ternary mixtures are accurate to 8 per cent and the carbon dioxide values are accurate to 6 per cent. The experimental reproducibilities for the isotherm data is approximately half the amounts indicated.

It was suspected during the planning stage and then confirmed during the ternary mixture experiments that the amount of hydrogen adsorbed would be too small to measure accurately with the system. However, it was apparent from certain of the high pressure-medium temperature experiments that an observable amount of hydrogen was being adsorbed. This was apparent because the first desorption-depressurization sample had a lower methane and carbon dioxide concentration than the feed gas. Attempts to calculate the amount of hydrogen adsorbed for several of the experimental tests indicated a quantity of the same order of magnitude as the measurement precision limits for the system. After this finding, the ternary mixtures were all computed with the assumption that the amount of hydrogen adsorbed was insignificant. Thus all adsorbates reported for binary and ternary gas mixtures are shown as binary solutions.

Pure Isotherms

The experimental pure isotherm values determined for methane and carbon dioxide are in Appendix E in Tables 6 and 8. The pure isotherms

were determined to approximately 100 PSIG for each of the gases at each of the three experimental temperatures.

It was decided to fit each of the data sets with a smooth function. This was to serve two purposes: first to determine the scatter of the data and second to provide a convenient tool for the calculation of pure isotherm values. A least-squares fitting program was used to find the best equation for each isotherm without any attempt at temperature correlation. The first function tried was a power series with the constraint that it must pass through the origin. For the six isothersm involved, it was found that six to nine terms were required with each of the fitted equations to reduce the deviations from the power series to the estimated accuracy for the data. The inconvenience of so many terms to achieve a merely acceptable approximation was cause to turn to other functional forms. The forms chosen were those which contain only two constants and have been successful in fitting other isotherms for heterogeneous adsorbents. The functions tried included:

$$N = \frac{N^* bP}{1 + bP} \qquad \text{(III-1)}$$

where N is the moles of adsorbate corresponding to a pressure P and N* is a nominal monolayer of adsorbate on the adsorbent. b is a constant for each isotherm.

$$\ell n\ N = k_1 + k_2\ \ell n\ P \qquad \text{(III-2)}$$

where k_1 and k_2 are constants to be solved for each data set.

$$\ell n\ N = k_1 + k_2\ \ell n\ (P_s/P) \qquad \text{(III-3)}$$

P_S is the component vapor pressure.

$$\ell n\ N = k_1 + k_2[\ell n(P_s/P)]^2 \qquad \text{(III-4)}$$

Equation (III-1) is the form of the Langmuir isotherm. The calculation for the constants was done by hand. It was found that the fit was very poor over the pressure range for all of the data sets. Equation (III-2) through (III-4) were least squares fitted with the use of a computer program which calculated the deviations for each of the individual input points and also computed an overall deviation criterion for the fitted equation based on the complete input set. The deviation function used was

$$\sigma = \left[\frac{\sum_i^k D_i^2}{k}\right]^{\frac{1}{2}} \qquad \text{(III-5)}$$

where D_i are the individual per cent deviations between input and calculated amounts adsorbed when pressure was used as the independent variable. The values used for P_s depend on the compound and the temperature and these values are shown in Table 2, Chapter V. Although the natural logarithm of the values for N and P or P_s/P were fitted, σ was also calculated after converting the calculated variables from the fitted equations to antilogarithms so they were in the same form as the original experimental data. Because of the nature of the logarithm function, values for deviations with the variables left as logarithms were extremely erratic when values for the logarithm arguments were near one.

The deviations for equation (III-2) were somewhat beyond the estimated accuracy for the isotherms. Most of the deviations with

equation (III-3) were within the estimated isotherm accuracy. The deviation criterion for equation (III-4) was half that for equation (III-3) and over 70 per cent of all of the points had deviations less than half the estimated isotherm accuracy. On this basis, equation (III-4) was found to give the best fits for all six methane and carbon dioxide isotherms. Values for k_1 and k_2 are presented in Table 5 in Appendix E. Values for P_s are in Table 2 in Chapter V. In this type of situation, when a function is found which satisfies all of the experimental data within the accuracy of each of the experimental points, nothing is gained by searching further for a function with less deviation. However, it must be noted that because a smooth fit is obtained does not necessarily prove anything of a general nature with respect to the fitted equation or the mechanisms involved.

The experimental points and the curve for the best-fitted equation for the methane and carbon dioxide isotherms are shown in Figures 3 through 8.

Hydrogen isotherms were determined and are presented in Figure 9. These values did not fit well on the characteristic curve to be discussed later. They were not used in connection with any of the prediction calculations. The accuracy of the hydrogen isotherm values is believed to be on the order of 9 per cent.

Mixture Isotherms

Unlike the pure isotherm experiments which produced a series of adsorption values and pressures for each test, a mixture isotherm experiment yields but one value each for methane and carbon dioxide at the pressure and temperature of the experiment. For the purposes of this

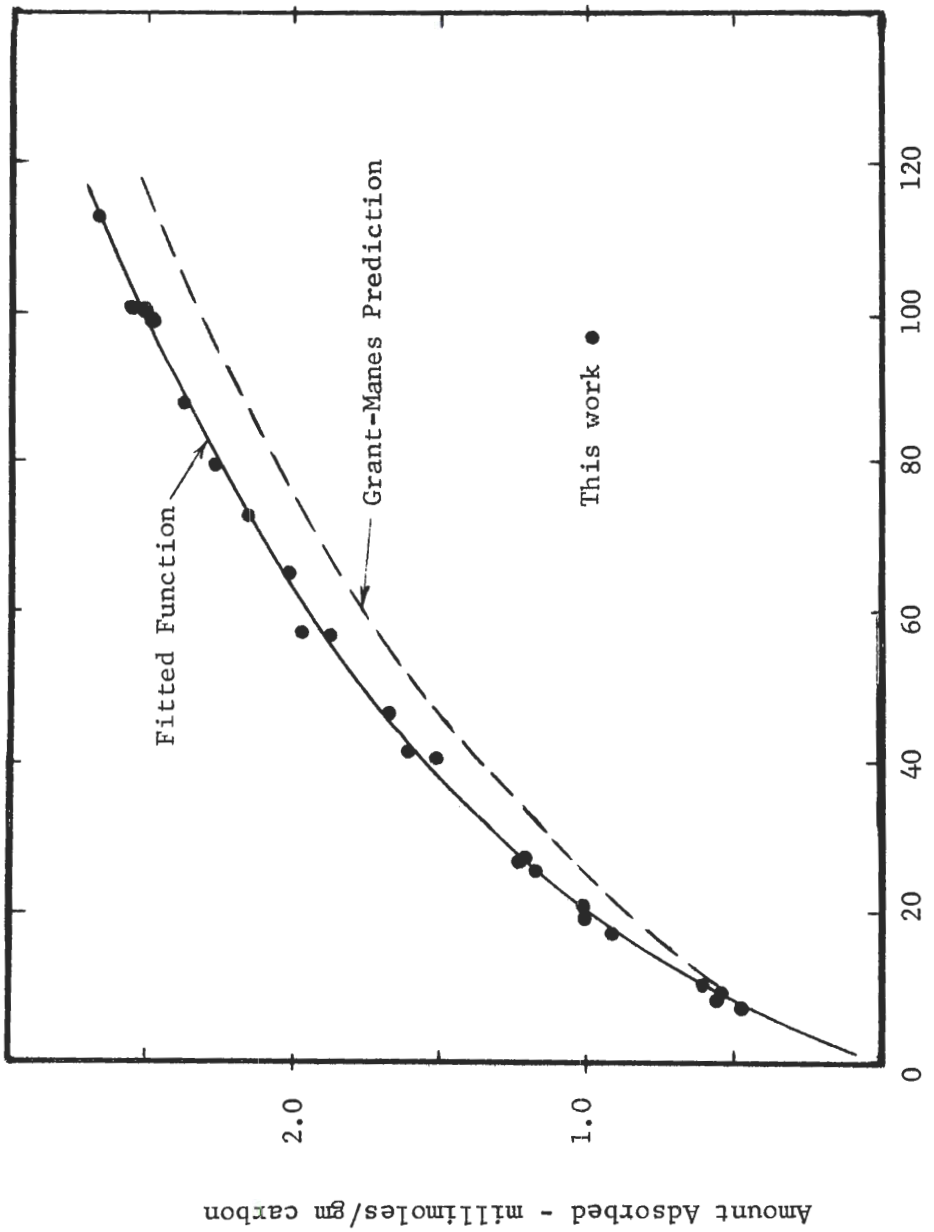

Figure 3. Methane Isotherm at 301.4 K

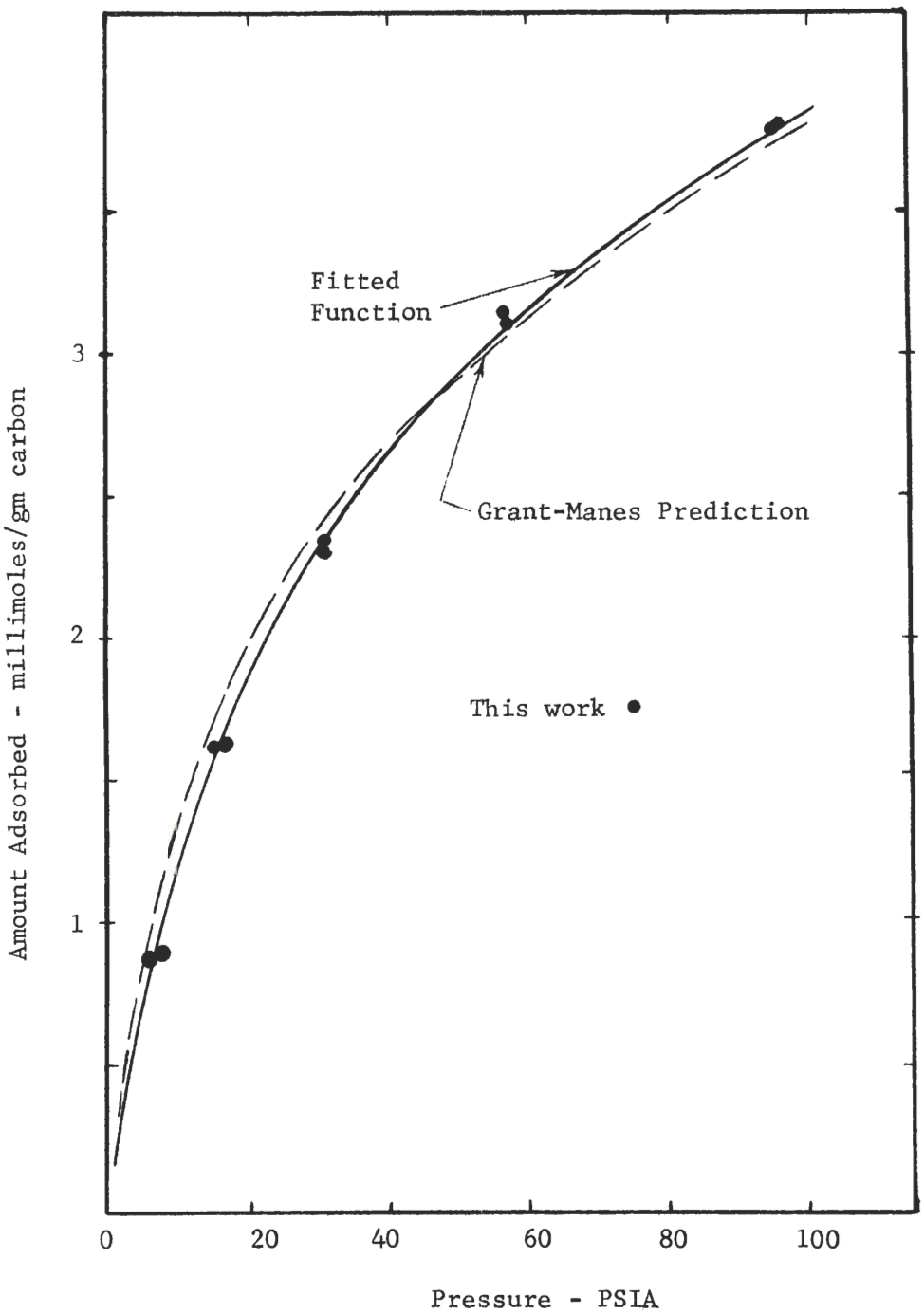

Figure 4. Methane Isotherm at 260.2 K

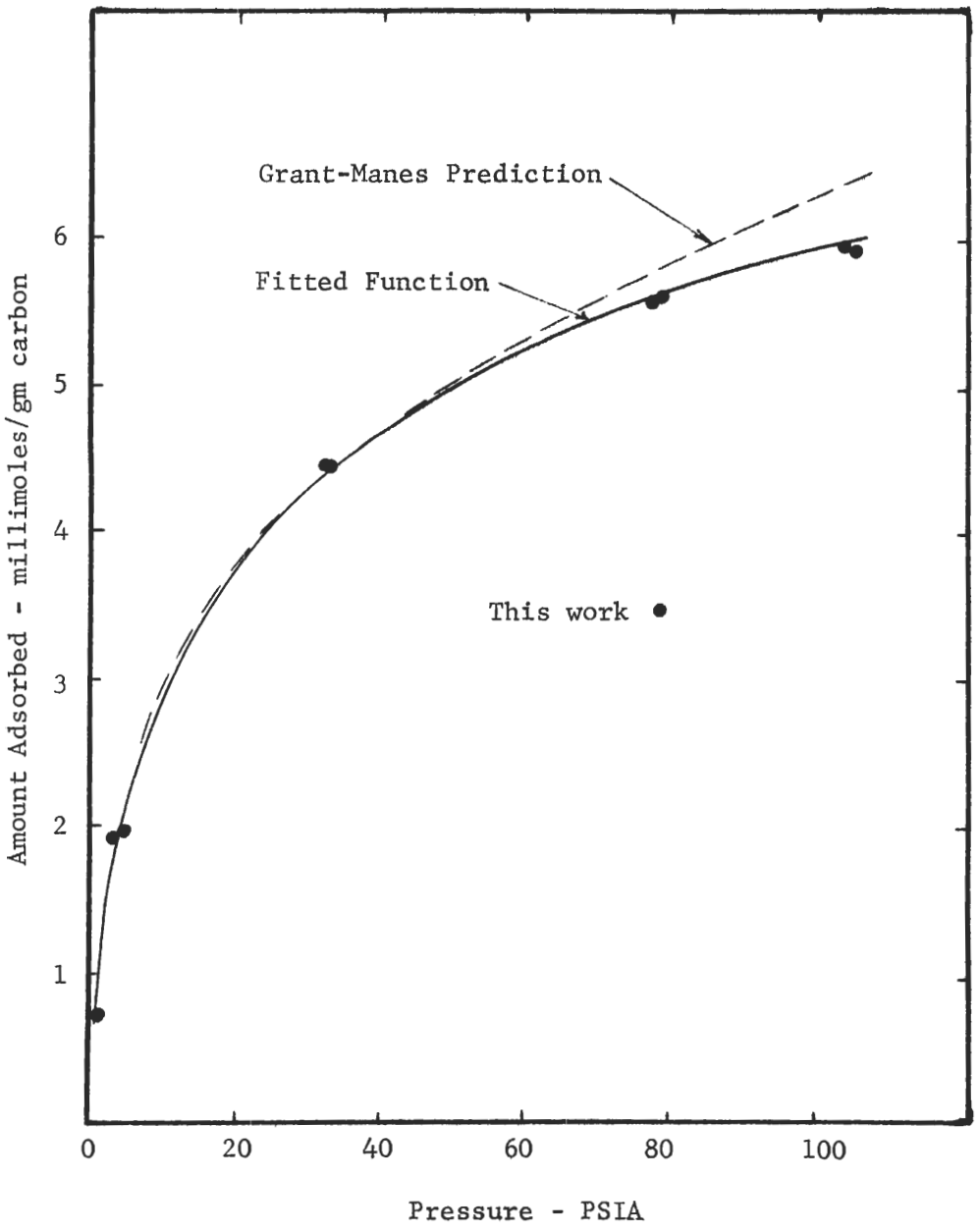

Figure 5. Methane Isotherm at 212.7 K

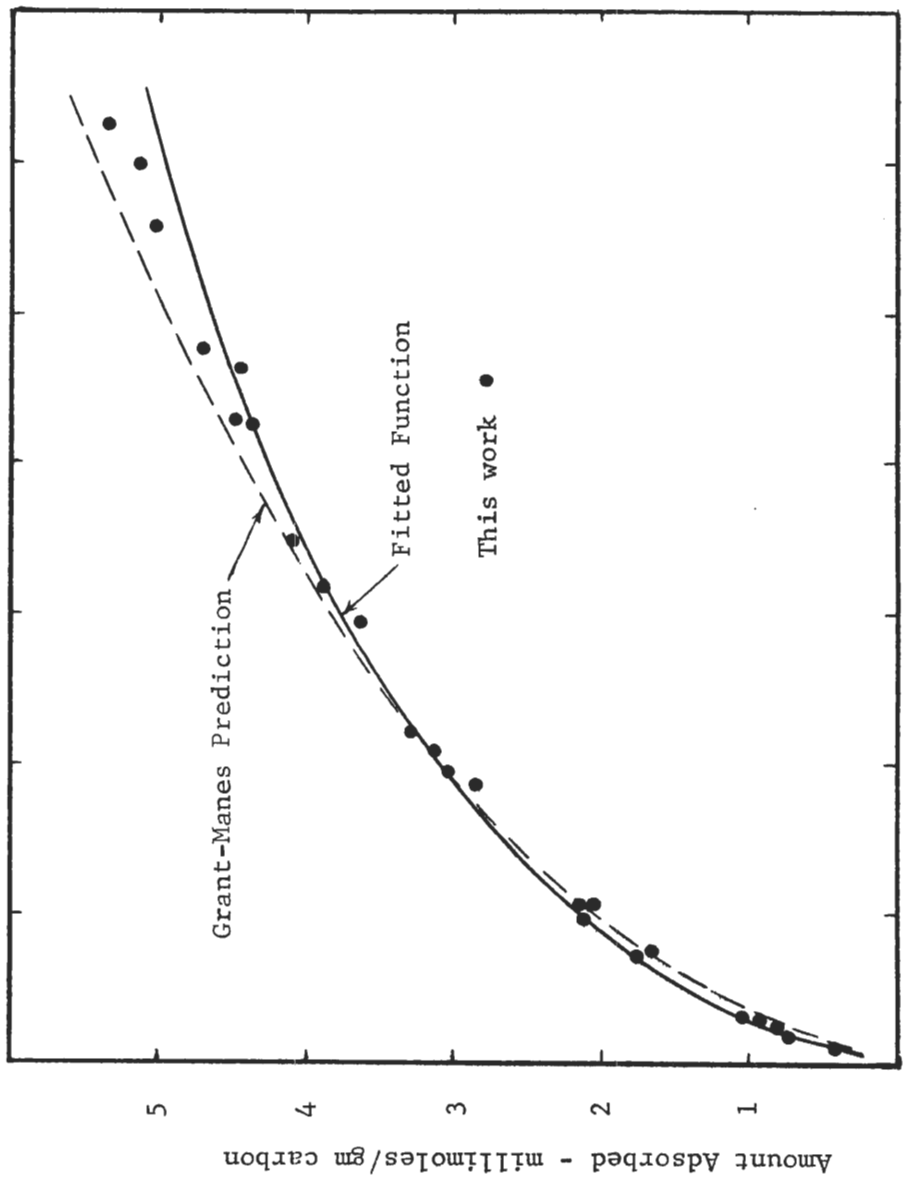

Figure 6. Carbon Dioxide Isotherm at 301.4 K

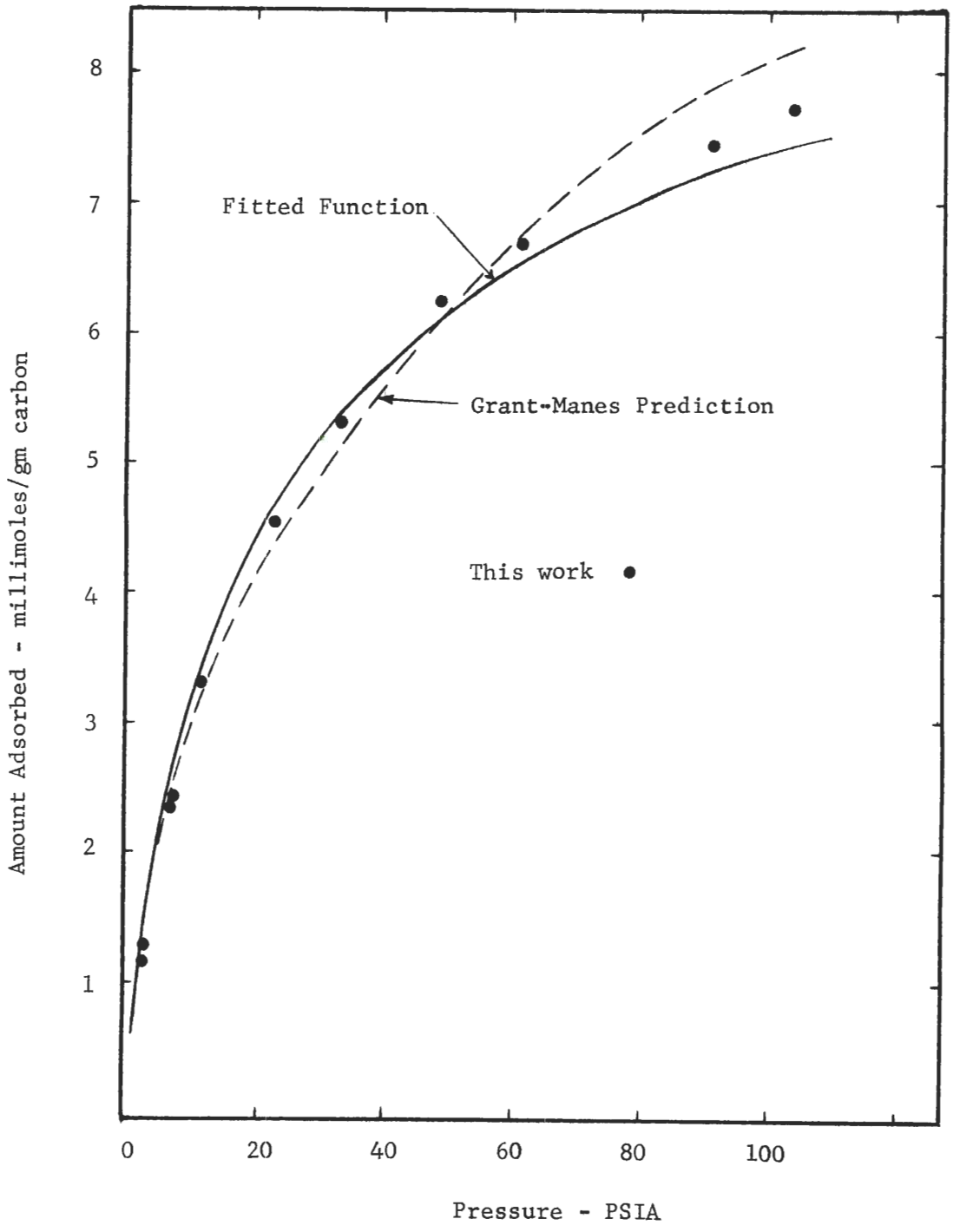

Figure 7. Carbon Dioxide Isotherm at 260.2 K

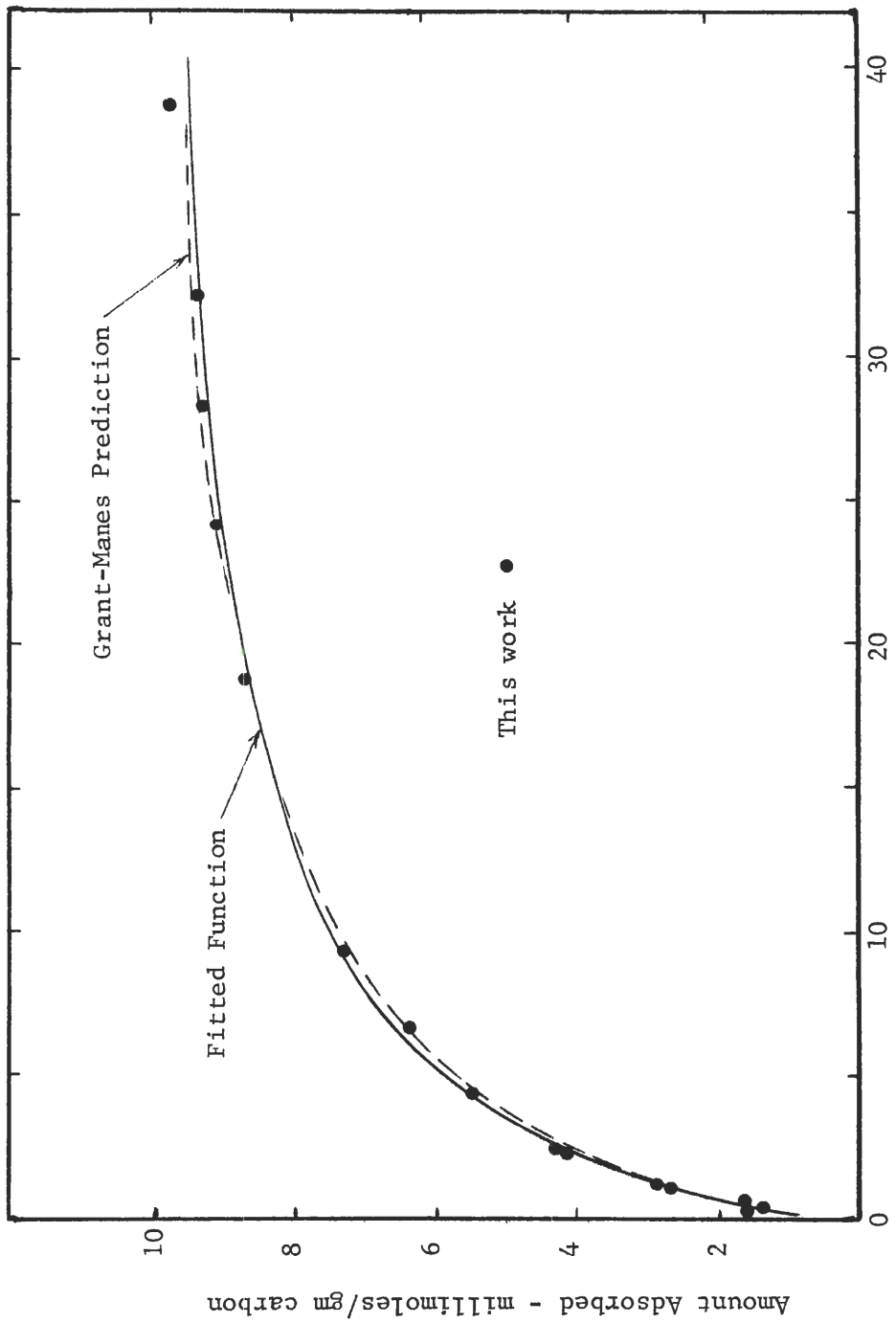

Figure 8. Carbon Dioxide Isotherm at 212.7 K

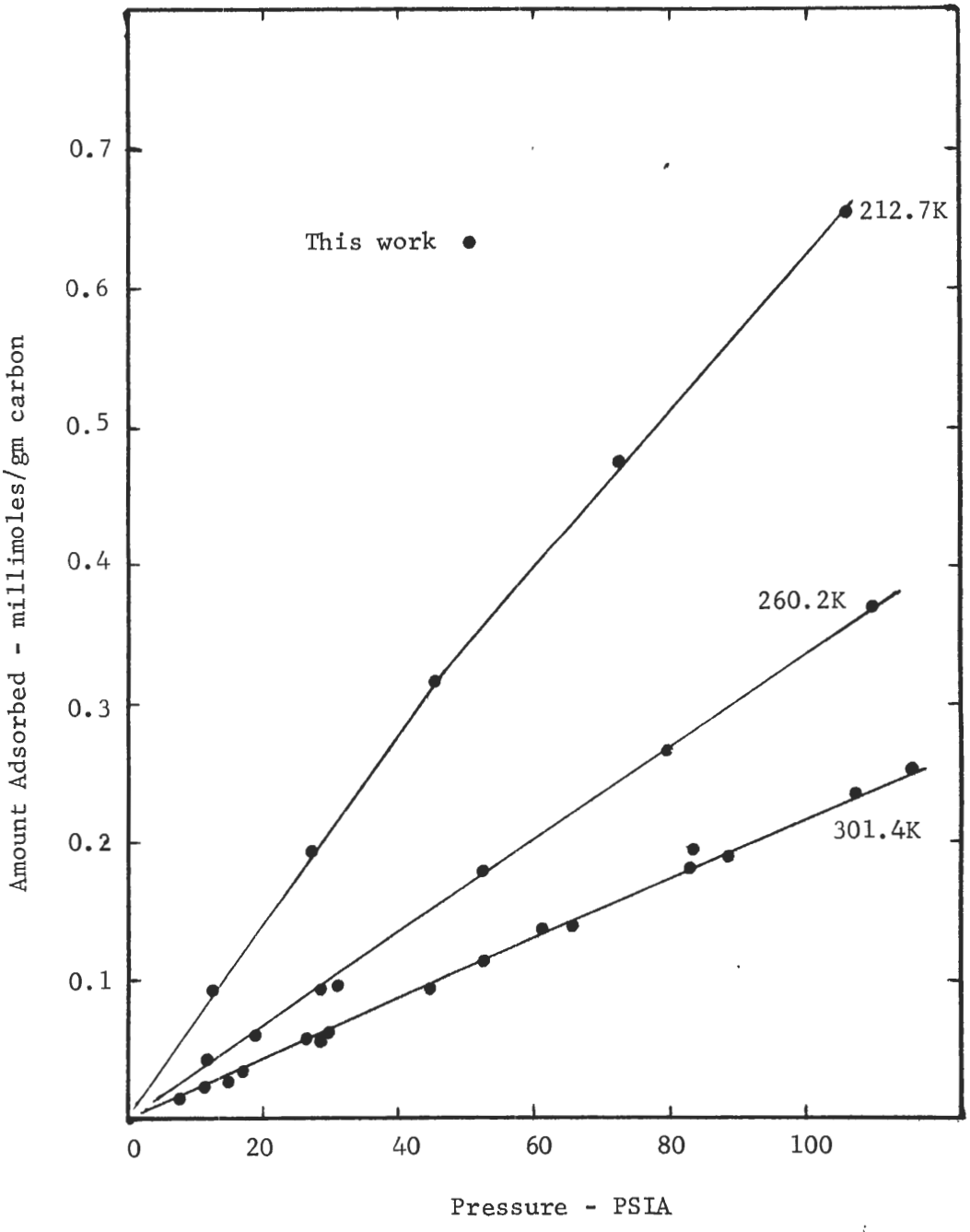

Figure 9. Hydrogen Isotherm at 301.4 K, 260.2 K and 212.7 K

investigation, it was thought that a minimum of three experiments would be sufficient to determine the mixture isotherms since the origin could be considered a fourth point. Some of the experiments were duplicated to learn experimental reproducibility and to verify that the adsorbent had not been affected by the experiments or insufficient regeneration.

The number of points obtained for the mixture isotherms was not sufficient to make curve fitting by a least squares procedure meaningful. The experimental values for mixture adsorption are presented in Appendix E in Table 10 for binaries and Table 11 for ternaries. These values are also shown graphically in Figures 11 to 23 in Chapter V in connection with the presentation of a prediction method.

Comparison of Results with Others

The pure methane and carbon dioxide isotherms were compared with the published results found by others. These checks were made in the region near 100 PSIA where differences would be most significant. Only the 301.4 K isotherms could be compared as no data were found for comparable carbons at the other temperatures. Even for the isotherms compared, a small amount of temperature interpolation was required with some of the sources.

The methane isotherm is essentially the same as that determined by Grant and Manes[21] who used the same carbon. It is below the capacity shown by Gonzalez[18] and Hasz and Barrere[22] who used a different proprietary activated carbon. The differences found were within the expectation after allowing for experimental error and carbon surface area.

The 301.4 K carbon dioxide isotherm was found to be below that of Hasz and Barrere[22] and approximately 3 per cent above the values shown

by Gonzalez[18]. Again the differences were within the allowances for experimental error and surface area.

No published adsorption values could be found for the binary or ternary gas mixtures covered in this investigation.

CHAPTER IV

THEORY

It has been recognized for many years that physical adsorption is the result of normal molecular interactions and is not caused by a special adsorption force. The major causes of such adsorption are known as "van der Waals" or dispersion forces. They are the same potentials which govern phase equilibrium and density functions for fluids. However, knowing that adsorption is not caused by a different type of force does not greatly simplify the problem. At least two or more species and three effective phases are present simultaneously in any adsorption system. Thus a model cannot be easily described with mathematical accuracy by the statistical thermodynamicist. Added to the complications are mobility of the adsorbate and the fact that a truly homogeneous surface on a molecular scale is almost impossible to achieve. The mathematical simulation of a heterogeneous surface is a far more involved problem. Thus the current preoccupation of the physical chemist is with systems which approach the ideal from a standpoint of mechanisms and shapes. For the adsorbate, monatomic or simple spherical molecules are preferred. For the adsorbent, a completely inert solid with a reasonably well understood lattice structure and a planar surface is chosen. These systems lead to a clearer picture of the detailed adsorption mechanism. They can also yield second virial coefficients when data are obtained in the very low pressure region where the isotherm follows Henry's Law which is:

$$N = kP \qquad \text{(IV-1)}$$

where N is the amount adsorbed, P is the absolute pressure and k is constant determined by experiment.

Polanyi Potential Theory

In 1916, Polanyi[34] developed a proposal which he had published two years earlier[33] that suggested a new avenue of attack on the problem. His theory related the amount adsorbed to a volume surrounding the absorbent. He restated his assumptions many years later in 1963 when he said[35]:

> Adsorption of gases on solids is due to an attraction that derives from a potential which is uniquely determined by the spatial position of the gas molecule and therefore independent of the presence of any other molecules in the field of adsorption potential. When subject to the field of adsorption, the gas behaves in accordance with its normal equation of state. When compressed to its "saturated" vapor density, it condenses to a liquid.*

In the 1916 paper, Polanyi included experimental verification for his theory. His adsorption potential was defined as the energy requirement for the transfer of one mole of component from the gas to the adsorbed phase. This energy requirement is essentially a work of compression given by

$$\epsilon = \int_{\bar{V}^G}^{\bar{V}^A} \bar{V} dP \qquad \text{(IV-2)}$$

Where ϵ is the adsorption potential $\bar{V}^G$ is gas phase molar volume and $\bar{V}^A$ is adsorbate molar volume. If the component follows the ideal gas equation of state, then the adsorption potential may be expressed as

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*The work 'saturated' above has been substituted for the word 'normal' which appears in the original text.

$$\epsilon = RT \ln(P_s/P) \qquad \text{(IV-3)}$$

where R is the gas constant and T a thermodynamic temperature. The adsorption potential was further asserted to be a unique function of the adsorbate volume $N\bar{V}$ for the particular adsorbent giving

$$\epsilon = F(N\bar{V}^A) \qquad \text{(IV-4)}$$

The explicit relation between adsorption potential and adsorbate volume is referred to as the characteristic curve for the adsorbent. Polanyi went on to postulate that there was a unique relation between the adsorption potential ϵ and the adsorbate density. He tried to allow for variations in the density of the adsorbate by assigning a series of zones within the adsorption volume. This technique made the construction of the characteristic curve an iterative procedure. The fact that Polanyi did not relate his theory to a particular mathematical form for the isotherm was the first strong point favoring his approach. The establishment of a basis for the effect of temperature on the adsorption isotherm was an additional factor which indicated the proposal was a significant contribution to adsorption theory.

Berenyi[1] in 1920 contributed to Polanyi Theory by showing how to use the van der Waals equation as a more accurate representation of the adsorbate density. Berenyi[2] also constructed many characteristic curves for different substances approaching but below the critical temperature. In 1927, Lowry and Olmstead[29] did a careful study of the Polanyi Theory using carbon dioxide data from various sources. They constructed many characteristic curves for carbon dioxide with different adsorbents. They constructed the first characteristic curve using data above and

below the adsorbate critical temperature.

Although construction of the Polanyi characteristic curve for an adsorbate-adsorbent combination was tedious because of the iterative procedures required to assign adsorbate density, it nevertheless seemed warranted as it offered the only route to learn the dependence of adsorption on temperature. Polanyi and Goldman[17] in 1928 showed the temperature invariance of the characteristic curve for each of four different compounds, all below their critical temperatures, using isotherms they determined at three or four different temperatures for each compound. A disagreement within the scientific community on the exact nature of the molecular forces in adsorption caused significant resistance to the acceptance of the Polanyi Potential Theory. By 1931, the nature of dispersion forces was better understood. In a survey paper at that time, Polanyi[36] related the adsorption potential to molecular polarizability and ionization potential or more approximately to the van der Waals constant 'a'.

Development of the Potential Theory

The Polanyi Potential Theory received only minor attention until after World War II when Dubinin and Timofeyev[11] noted that characteristic curves for different substances on the same adsorbent had similar shapes. They suggested that the adsorption potential should be defined as

$$\epsilon = \frac{F(N\bar{V}^{A})}{\beta} \qquad \text{(IV-5)}$$

where β was called the affinity coefficient and was understood to be a property of the adsorbate. This relationship defined a new characteristic

curve explicitly relating ϵ to the volume of adsorbate per unit of adsorbent. This new adsorption potential allowed a single characteristic curve to show many adsorbed substances on the same adsorbent. This new definition of the adsorption potential in effect advanced the Potential Theory of Polanyi to the point of saying that equal adsorbed volumes for different adsorbed substances would have equal adsorption potentials. Dubinin and Timofeyev went on to establish experimental proof for their equi-potential modification of the Polanyi Potential Theory by graphically determining values for a group of sixteen compounds below their critical temperature on two carbon adsorbents. They also determined β values for three compounds from isotherms published by others. As a part of this same work, they studied several physical properties and attempted to correlate them with the values found for β. Their recommendation was that the adsorbate molar volume was the best property to use for the affinity coefficient.

In 1950, Lewis et al.[27] made a series of adsorption studies. In attempting to correlate their data, they found most of the theories which included specific isotherm equations failed to fit their results. In studying the Polanyi Theory, they noted that the Polanyi adsorption potential was actually a Gibbs free energy change for the adsorbate from the gas to the condensed phase. Thus the same adsorption potential for two adsorbates would be

$$N_1 RT \ln(P_s/P)_1 = N_2 RT \ln (P_s/P)_2 \qquad \text{(IV-6)}$$

which is equating the free energies for the amounts adsorbed per unit amount of adsorbent. Then noting the adsorption Potential Theory

requirement for equal volumes of adsorbate at equal potentials, they wrote

$$N_1\bar{V}_1^A = N_2\bar{V}_2^A \qquad \text{(IV-7)}$$

Dividing equation (IV-6) by equation (IV-7) gave a definition for the adsorption potential consistent with the recommendation of Dubinin and Timofeyev[11]. Because all of their adsorption data was at the same temperature, they also divided their adsorption potential by RT giving

$$\epsilon_i = \frac{1}{\bar{V}_i} \ln (P_s/P)_i \qquad \text{(IV-8)}$$

This particular approach to the adsorption potential clearly requires the same adsorbate molar volume value $\bar{V}$ to be used for the ordinate and abscissa of the characteristic curve. This constraint does not apply to the Dubinin approach to Adsorption Potential Theory as indicated in equation (IV-5). Because equation (IV-6) should use fugacities instead of pressures to be thermodynamically correct, the relation for the adsorption potential was modified by Lewis et al.[27] to

$$\epsilon_j = \frac{1}{\bar{V}_j} \ln \left(\frac{f_s}{f}\right)_j \qquad \text{(IV-9)}$$

They plotted adsorption potential ϵ_j as the abscissa and $N_i\bar{V}_i$ as the ordinate for their 8 pure hydrocarbon isotherms on two different activated carbons. The isotherms were at the same temperature. One of the hydrocarbons, methane was above its critical temperature and all of the rest were below.

Two methods were tried for the ordinate, $N\bar{V}$, of the characteristic

curve. When the saturated liquid molar volume at the temperature of the isotherms was used for the adsorbates, separate curves were found. When a molar volume equal to that of the saturated liquid at the adsorption pressure was used, a single characteristic curve for each of the two carbons resulted. However, these curves did divide at the low pressure and into two separate curves for the saturated and unsaturated hydrocarbons with each of the carbons.

In 1962, Grant et al.[19] determined isotherms for five different paraffinic hydrocarbons at three different temperatures on Pittsburgh BPL carbon above and below the critical temperatures. Using an adsorbate molar volume equal to the saturated liquid density at adsorption pressure, they were able to construct a single characteristic curve for all five compounds. Later Grant and Manes[20] extended the study to nitrogen, argon and other gases for temperatures above and below the critical at low pressures. It was found that hydrogen and neon did not correlate with the other materials. Otherwise a single curve was satisfactory for all of the data. In this work they used an adsorbate molar volume equal to the saturated liquid at the normal boiling point for both the abscissa and ordinate variables for the entire range of data.

The possibility that a single characteristic curve could be constructed which would establish the effect of temperature on the adsorption isotherm and allow the prediction of isotherms for pure components based on their physical properties gave a new impetus to study of the Adsorption Potential Theory. The empirical assignment of adsorbate molar volume seems the key to a direct method for reducing the Adsorption Potential Theory to a practical procedure.

A characteristic curve constructed from the pure methane and carbon dioxide isotherms of this study is presented as Figure 10. This figure shows adsorbate volume per unit of adsorbent as the ordinate. For this plot the adsorbate molar volumes used in both ordinate and abscissa are the values corresponding to that of the saturated liquid at its normal boiling point. The value for N in the ordinate is milligram-moles per gram of adsorbent calculated from the fitted isotherm equations at pressure increments. The pressure was converted to fugacity in a subroutine of the Fortran program used for calculation of the corresponding adsorption potential. The adsorption potential is shown divided by the constant R. All of the characteristic curves in this work use an adsorption potential which does not include the gas constant R. All of the values used to compute the variables for Figure 10 are presented in Table 2 in Chapter V and in Appendix E.

The adsorption coverages used for the calculated variables computed in the construction of Figure 10 are the same as the ranges of the isotherm experiments. The plotted points of this Adsorption Potential characteristic curve show an overlapping of the six data sets. This overlapping occurs with respect to the two different species and temperatures for the data sets.

In 1969, Hasz and Barrere[22] determined adsorption data for a series of hydrocarbons and carbon dioxide at the single temperature of 77°F on activated carbon. They constructed a single characteristic curve using adsorbate molar volume of liquid at the normal boiling point with a correction factor which they determined empirically as a function of the reduced temperature.

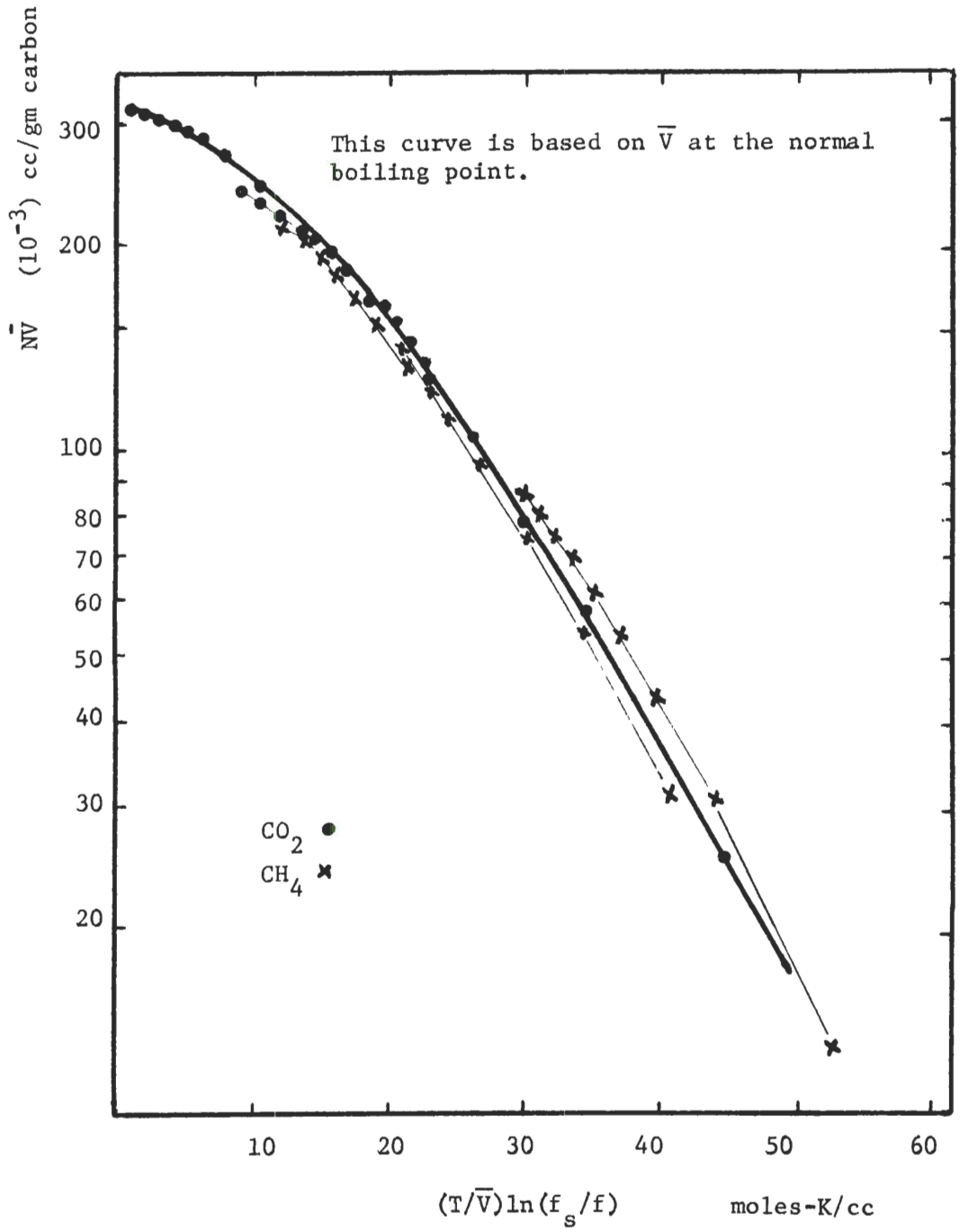

Figure 10. Adsorption Potential Theory Characteristic Curve.

Tolles et al.[40] carried out a study on the adsorption of six compounds below their critical temperature on various heterogeneous carbon adsorbents including Pittsburg type BPL. They correlated affinity coefficient with molar refraction, polarizability, molar parachor, and liquid molar volume at the adsorption temperature. They found that the parachor was slightly better than molar volume as Dubinin et al.[10] had found in the earlier work.

Applications of Polanyi Theory to Mixtures

In 1965, Grant and Manes[21] studied adsorption of binary mixtures of methane as the major component with 2 per cent or less propane, butane, or hexane to 1000 PSIA on Pittsburgh BPL carbon. They determined all the mixture isotherms at 25°C which is above the critical for methane and below that for all the other components. Following the writings of Dubinin which asserted that the adsorption potentials for all components must be equal at equilibrium within a system, they applied the Lewis-Randal fugacity rule to equation (IV-9) and divided by temperature to obtain

$$\frac{1}{\bar{V}_1} \ell n\left(\frac{Xf_s}{f}\right)_1 = \frac{1}{\bar{V}_2} \ell n\left(\frac{Xf_s}{f}\right)_2 \qquad \text{(IV-10)}$$

When the pressure, temperature, gas phase composition and molar volumes for saturated liquid absorbate are known, equation (IV-10) may be solved for the adsorbate composition of a binary because

$$X_1 + X_2 = 1 \qquad \text{(IV-11)}$$

Grant and Manes used an empirical definition for a pseudo-pressure

$$P_{gi} = P\left(\frac{Y}{X}\right)_i \qquad \text{(IV-12)}$$

and employed saturated liquid molar volumes at a pressure equal to P_g. As a prediction method, this would require iteration between equations (IV-10) and IV-12). After solving equation (IV-10) for adsorbate composition, the molar volume of the mixed adsorbate was calculated by a linear mixing relation

$$X_1\bar{V}_1 + X_2\bar{V}_2 = \bar{V}_{mx} \qquad \text{(IV-13)}$$

Then using an adsorption potential characteristic curve constructed from isotherms for five pure paraffin hydrocarbons at various temperatures, they multiplied the value of the terms in equation (IV-10) by the temperature of the mixture to obtain an abscissa value for the characteristic curve. The ordinate was then divided by the molar volume for the mixed adsorbate from equation (IV-13) to find the total number of moles of adsorbate. This quantity with the adsorbate mole fractions solved earlier gave a complete solution to the prediction problem.

For this investigation, after establishing that the mixed adsorbate characteristic curve was essentially the same as the characteristic curve constructed from the pure methane and carbon dioxide isotherms, the above method was used for mixture prediction. In addition to calculating the adsorption potential at a molar volume equal to saturated liquid at P_g, the earlier Grant-Manes method[20] of using the molar volume for the saturated liquid at the normal boiling point was tried. This latter variation was found fully as successful. This will be discussed further in Chapter V. Using the saturated liquid molar volume at the normal

boiling point eliminates the need for iteration from the prediction procedure.

Fernbacher[15] used an Adsorption Potential Theory characteristic curve to predict the amount of adsorbate for the helium-nitrogen system on Pittsburgh BPL carbon at 100 K and 150 K to 100 atmospheres. This was above the critical temperature for helium and below that for nitrogen.

Other Modifications of the Potential Theory

In studying characteristic curves for various pure substances on heterogeneous adsorbents, Dubinin and Radushkevich[13] noted that a Gaussian distribution of the adsorption potential seemed to be indicated. They asserted that the isotherm should be closely represented by

$$W = W_o \exp - [k\epsilon^2] \qquad \text{(IV-14)}$$

where W is the adsorbate volume at an adsorption potential corresponding to ϵ, W_o the maximum adsorbate volume for the adsorbent and k a constant. As a result of the work by Dubinin and Timofeyev[12], they later modified[14] equation (IV-12) to

$$N = \frac{W_o}{\bar{V}} \exp - [\frac{BT^2}{\beta^2} (\ell n \frac{P_s}{P})^2] \qquad \text{(IV-15)}$$

which is subsequently referred to as the Dubinin-Radushkevich (D-R) equation. W_o and B are parameters characteristic of the adsorbent. For materials below their critical temperatures and low pressures, they found excellent correlations using this equation in logarithmic form. As a model for the molar volume, Dubinin and Nikolaev[31] developed an equation dependent upon the adsorption temperature. The adsorbate molar volume was considered to be a linear function of temperature

between the normal boiling point and the critical point. The value used for molar volume at the critical temperature is

$$b = \frac{RT_c}{8\ P_c} \qquad \text{(IV-16)}$$

which is a method used to compute van der Waals 'b'. Above the critical temperature, the molar volume was considered a constant equal to b. Below the normal boiling point, best values for the saturated liquid molar volume were used corresponding to adsorption temperature.

Dubinin and Nikolaev[31] extended their adsorption investigations to substances above the critical temperature. As a result of these studies, they modified the D-R equation to

$$N = \frac{W_o}{b} \exp - \left[\frac{BT^2}{\beta^2} \left(\ell n \frac{T_R^2 P_c}{P}\right)^2\right] \qquad \text{(IV-17)}$$

where T_R is the reduced temperature.

The later work of Dubinin[3] indicated that the D-R equation had limitations for application to adsorption. It can be seen that the function does not reduce to Henry's Law at low pressure. This is a statistical mechanics requirement for any isotherm equation. Dovaston et al.[9] found good agreement using the D-R equation to 600 Torr with pure carbon dioxide isotherms from 195 K to 298 K. However, this equation failed to represent the data below P/P_s equal to 10^{-3}. Steele[39] has shown that the D-R equation can be derived using statistical mechanics with a particular set of initial assumptions.

Dubinin[10] recognized that the D-R equation does not apply to heterogeneous adsorbents of a structural type different from typical activated carbon; i.e. one with larger pores. For the case of adsorbents

with larger pores which Dubinin calls the second structural type, the isotherm proposed is

$$N = \frac{W_o}{\bar{V}} \exp - [\frac{BT}{\beta} \ell n \frac{P_s}{P}] \qquad \text{(IV-18)}$$

As in the D-R equation, W_o and B are parameters related to the adsorbent and β is dependent upon the adsorbate. Equation (IV-18) is for use below the critical temperature of the adsorbate.

The D-R equation has been applied by Bering et al.[5] to binary mixture adsorption with both components below their critical temperatures and at low pressures. They suggested the D-R isotherm to predict the total amount of adsorbate. The values for W_o and B are characteristic of the adsorbent. They used linear mixture rules for the molar volume, equation (IV-13), and for β_{mx}

$$\beta_{mx} = X_1\beta_1 + X_2\beta_2 \qquad \text{(IV-19)}$$

Values of P_s and P are obtained by summing the individual components. To solve for the composition of the mixed adsorbate, they made use of an empirical relation found by Lewis et al.[28] which is

$$X_i = \frac{N_i(Y_iP,T)}{N_i^o(P,T)} \qquad \text{(IV-20)}$$

Use of equation (IV-20) does not satisfy equation (IV-11) for many systems as was found in this investigation and has been reported by others[8, 21]. This is shown in Tables 12 and 13 in Appendix E.

It is recognized that none of the methods described to obtain a value for molar volume results in a quantity which can be accepted as representing the true density of the adsorbed phase. The direct

measurement of actual adsorbate density is not possible by the conventional adsorption techniques which have been described previously. Bering et al.[4] used a special combination gravimetric-volumetric procedure to measure adsorption in the water-ethyl chloride system. Their measurements indicated that adsorbed water had a density one and one quarter times the normal liquid value. Because the Adsorption Potential Theory, as modified, uses molar volume for the adsorbate in both the ordinate and the abscissa of the characteristic curve, it is entirely possible that there are compensating errors with a particular empirical method. Such compensating errors may overshadow a very complex mechanism involving relations not yet understood. Thus the success of a method cannot be regarded as sufficient proof that the conditions of the empirical procedure are an explicit indication of the physical reality.

CHAPTER V

PREDICTION RESULTS

The adsorption data obtained as a part of this investigation are in a somewhat different domain from mixture experiments reported by others. The binary and ternary gas solutions studied contained one component below its critical temperature and the remaining gas or gases above. The partial pressures of the adsorbed components were to 50 PSIA which is higher than attained in most other studies. The same mixtures were studied at several temperature levels. The binary mixtures were related to the ternary mixtures by having the adsorbed components in the same molar ratios. The same adsorbent was used for all experiments to eliminate the variables related to heterogeneous adsorbents.

Prediction methods proposed by others were studied to assess those which might be expected to give the best results with the components and conditions of this study. As a minimum requirement a particular method would be expected to allow the prediction of the amount of each component adsorbed from a specified gas mixture using only the pure material isotherms on the same adsorbent at a particular pressure and temperature. Of all methods available, only those related to the Polanyi Potential Theory allow prediction at temperatures different from those of the pure isotherm data. With this method, the effect of temperature is known directly within the definition of the adsorption potential. While the procedures for the application of the Potential Theory are largely empirical, the method is still sufficiently fundamental to

allow the prediction for adsorption of substances for which no pure isotherms are available. Once a workable molar volume relation is established for the adsorbate, a characteristic curve constructed from any typical adsorbate suffices to allow the prediction of adsorption for different substances on the same adsorbent.

The work of Grant and Manes[21] seemed the most comprehensive and pertinent to the purposes of this study. They demonstrated their modification of the Polanyi Theory with binary mixtures composed of one component above and the other below the critical temperature. It remained to extend their work to higher partial pressures for all components and to several temperature levels.

The work of Bering et al.[5] with the application of the D-R equation to mixtures seemed worthy of study since several advantages beyond the basic Polanyi Theory are obtained. The construction of a characteristic curve is unnecessary. A definitive Polanyi characteristic curve may require data over a wide pressure range or at several temperatures. The D-R equation parameters can theoretically be solved with two adsorption values which will characterize the adsorbent. The parameter for the characterization of the adsorbate can be assigned based on physical properties. Results from this model are discussed later in this chapter. Several other classic models were checked and are presented in this chapter.

Adsorbate Physical Properties

A number of physical properties were required for the necessary calculations in connection with the study of the Polanyi Theory and the D-R equation. Liquid density and vapor pressures for methane were taken

from the monograph of Zaguruchenko and Zhuralev[43]. The values used for carbon dioxide were from data determined by Meyers and Van Dusen as reported in the monograph of Quinn and Jones[37]. The fugacity for for saturated methane above the critical temperature was required for the three experimental temperatures. This is hypothetical quantity which was calculated by assuming a linear relation between 1/T and $\ell n(P_s)$. The normal boiling point and the critical point were used to define the linear relationship. The pseudo-vapor pressure from this assumed relation was then used in a relation based on the BWR equation given by Orye[32] to calculate the fugacity directly after solving the vapor density by iteration.

While the calculation of pseudo-vapor pressures above the critical temperature was not required for the carbon dioxide, it was required to use the same linear relation to determine a normal boiling point for this compound. The method described above was employed with the critical and triple points used to determine the linear relationship. The normal boiling temperature indicated by this relation was used with liquid densities reported by Quinn and Jones[37] at higher pressures to select the molar volume at the calculated normal boiling point. The physical properties chosen and the calculated fugacities are shown in Table 2.

Pure Isotherm Prediction

Using the Polanyi Potential Theory as applied by Grant and Manes[20, 21] the six fitted isotherm equations for methane and carbon dioxide were used to construct a characteristic curve showing $(N\bar{V})_i$ plotted against $T/\bar{V}_i \ell n(fs/f)_i$. Because Grant and Manes had used two

Table 2. Adsorbate Physical Properties

	Methane	Carbon Dioxide
$\bar{V}$ at the normal boiling point, cc/gm-mole	37.7	33.2
van der Waals "b" in cc/gm-mole	42.7	42.8
Ps in PSIA at 301.4 K	4914.7	1004.1
at 260.2 K	2853.3	352.4
at 212.7 K	1177.6	57.7
Fugacity in PSIA at 301.4 K	3513.7	668.1
at 260.2 K	1768.9	284.3
at 212.7 K	716.2	54.05
Critical Temperature Tc, K	190.7	304.3
Critical Pressure, PSIA	673.2	1073.

different methods to arrive at a value for the absorbate molar volume, both methods were used in this study to determine which would give the better predicted results. The preferred method, based on the mixture findings to be discussed later in this chapter, assumed that the adsorbate molar volume was equal to the saturated liquid at the normal boiling point. The curve based on this method is presented as Figure 10 in Chapter IV. The characteristic curve which uses a variable molar volume at the empirical saturation pressure given by equation (IV-12) is shown in Appendix E as Figure 29. Grant and Manes[21] suggest the use of constant adsorbate molar volume in the adsorption potential variable while using the variable molar volume for the adsorbate volume variable of the characteristic curve to simplify the method. This study used the same value for adsorbate molar volume in the abscissa and ordinate of each of the two methods.

The hydrogen isotherms were also used to calculate the Polanyi characteristic curve variables. It was found that the three hydrogen isotherms gave characteristic curve values which fell into three isolated regions all separate from the eye-fitted characteristic curve defined by the methane and carbon dioxide isotherms. It was later found that none of the calculations in this investigation required characteristic curve values outside of the range defined by methane and carbon dioxide. Thus the hydrogen isotherm values were not used in any prediction method computations.

As a first check on the Grant-Manes prediction method, the characteristic curve shown in Chapter IV as Figure 10 was used to predict the six pure isotherms. This was done by approximating the solid line

in Figure 10 over the full range shown by four straight lines. The equations for these lines were included in a Fortran program which calculated methane and carbon dioxide adsorption values for a series of pressures at the desired temperatures. The predicted isotherms based on this procedure are shown on Figures 3 to 8 in Chapter III. With the exception of the carbon dioxide isotherm at 260.2 K in the higher pressure portion, the predicted curves are all in good agreement with the experimental data.

Because equation (III-4) was the relationship which gave the best fit for all six sets of isotherm data and this is the same form as the D-R equation (IV-15), it was anticipated that good results should be obtained from this modification of the Polanyi Theory. If the D-R equation was to serve as a general temperature invariant isotherm for methane and carbon dioxide, then the k_2 constant from equation (III-4) which had already been determined for the individual isotherms could be analyzed to learn if B/β^2 was a constant as indicated by Dubinin[10] for an adsorbent of the activated carbon type. The value for k_2 was divided by the square of the temperature for all of the isotherm equations and the results are presented in Table 3.

Table 3. Dubinin-Radushkevich Dimensionless Variables Calculated from Isotherm Equations for Methane and Carbon Dioxide

Isotherm	$\frac{k_2}{T}$ (10^4)	$B/\beta^2 = \frac{k_2}{T^2}$ (10^2)
Methane at 301.4 K	2.01	6.05
at 260.2 K	2.03	5.28
at 212.7 K	2.06	4.38
Carbon Dioxide at 301.4 K	2.62	7.88
at 260.2 K	2.94	7.65
at 212.7 K	3.79	8.05

It will be seen that the values shown for B/β^2 are constant within experimental error for the carbon dioxide isotherms. However, they are not the same value for methane. The results from dividing k_2 by the experimental temperature are also shown in Table 3. For this quantity, the three methane values are surprisingly close to each other. This value is comparable to BT/β and would indicate that equation (IV-18) is the proper isotherm based on the writings of Dubinin. But equation (IV-18) is for an adsorbent of the non-microporous type and this conclusion is unacceptable for the carbon used. This inconsistency led to the conclusion that more development is required before applications of the type under consideration can be made with the D-R equation and related relations. The mixture results were tried with the D-R equation and these will be discussed later in this chapter.

Mixture Isotherm Prediction

Characteristic curves were constructed from the experimental isotherm data for methane and carbon dioxide at all three temperatures and over the entire pressure ranges tested. The hydrogen isotherm results

fell in a different region and were not included in the constructed characteristic curves.

The curves were constructed using the molar volume for the adsorbate corresponding to saturated liquid at the normal boiling point and also at pseudo-pressures Pg defined by equation (IV-12). The characteristic curve based on normal boiling point liquid molar volume is Figure 10 in Chapter IV. The other characteristic curve is Figure 29 shown in Appendix E. Each curve was re-drawn on separate plots to which the experimental mixture results were added. Equation (IV-13) was used for the molar volume of the binary adsorbate. The adsorption potential was calculated for each methane and carbon dioxide data point using each of the two molar volume methods. Separate plots were used for the binary and ternary data with each molar volume method giving four plots. These are presented as Figures 30 to 33 in Appendix E. Most of the mixture isotherms consist of three to five points. The points for these individual sets are connected by fine lines. The results is a graphical presentation of the agreement between the "best" characteristic curve defined by mixture adsorption results and the characteristic curve constructed solely from pure isotherms for the mixture components.

The degree of agreement between the pure and mixture characteristic curves may be taken as a direct indication of the degree of success expected for the prediction method which governed the characteristic curve construction. This was the purpose for constructing plots by use of the two adsorbate molar volume methods.

The ternary mixture plots, Figures 32 and 33, showed no clear

superiority of one method over the other. The binary plots, Figures 30 and 31, indicate a slightly better agreement using a molar volume corresponding to saturated liquid at the normal boiling point. After finding that this method was slightly superior, this was the procedure used for all subsequent calculations. Making use of Equation (IV-11), Equation (IV-10) was first solved by iteration to give the adsorbate composition. Then using the same linear equation for the characteristic curve as had been used for predicting the pure component isotherms as described above, a value for $N_T\bar{V}_{mx}$ which corresponded to an adsorption potential equal to $T/\bar{V}_i \ln(\frac{Xf_s}{f})_i$ was found. Knowing the mixture adsorbate molar volume from equation (IV-13) allowed the total amount adsorbed to be computed. The adsorbate composition from the first calculation step was then used to give the amount of each component adsorbed. Temperature and gas mixture composition were used as inputs to this program which then calculated the amount of methane and carbon dioxide adsorbed for a series of pressures. This program was used to calculate the predicted isotherm for the temperatures and mixtures corresponding to the experimental data. The predicted isotherms and the experimental points determined in this investigation were put on the same plot for the 13 mixture-temperature combinations studied. These plots are shown as Figures 11 to 23.

Conclusions based on these plots are presented in Chapter VI.

Although the number of experimental points determined for the mixture isotherms was too few to allow least squares fitting, attempts were made to check the data with some of the isotherm functions which have been found useful by others for mixtures.

To learn how well the D-R equation would fit the isotherms for

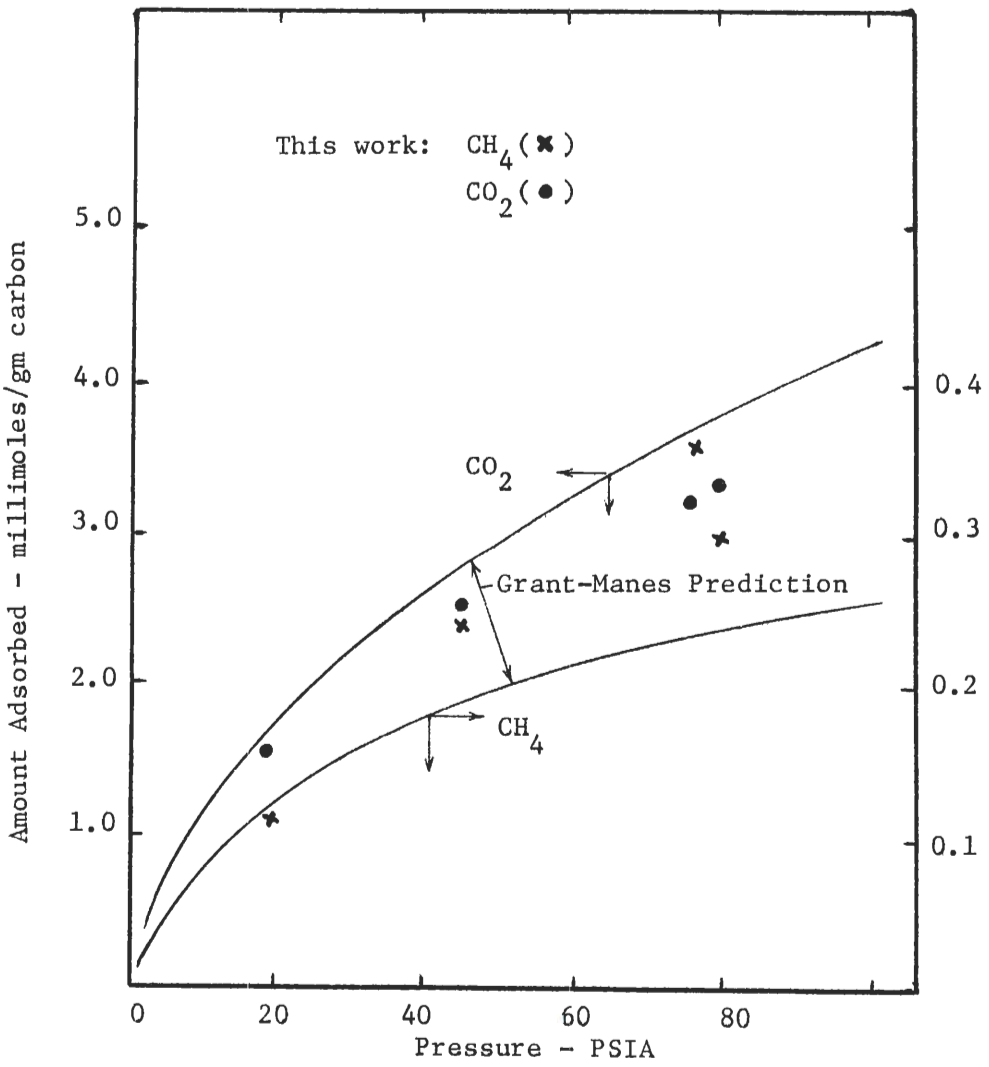

Figure 11. Methane (18.8 Mole %) - Carbon Dioxide (81.2 Mole %) Isotherm at 301.4 K.

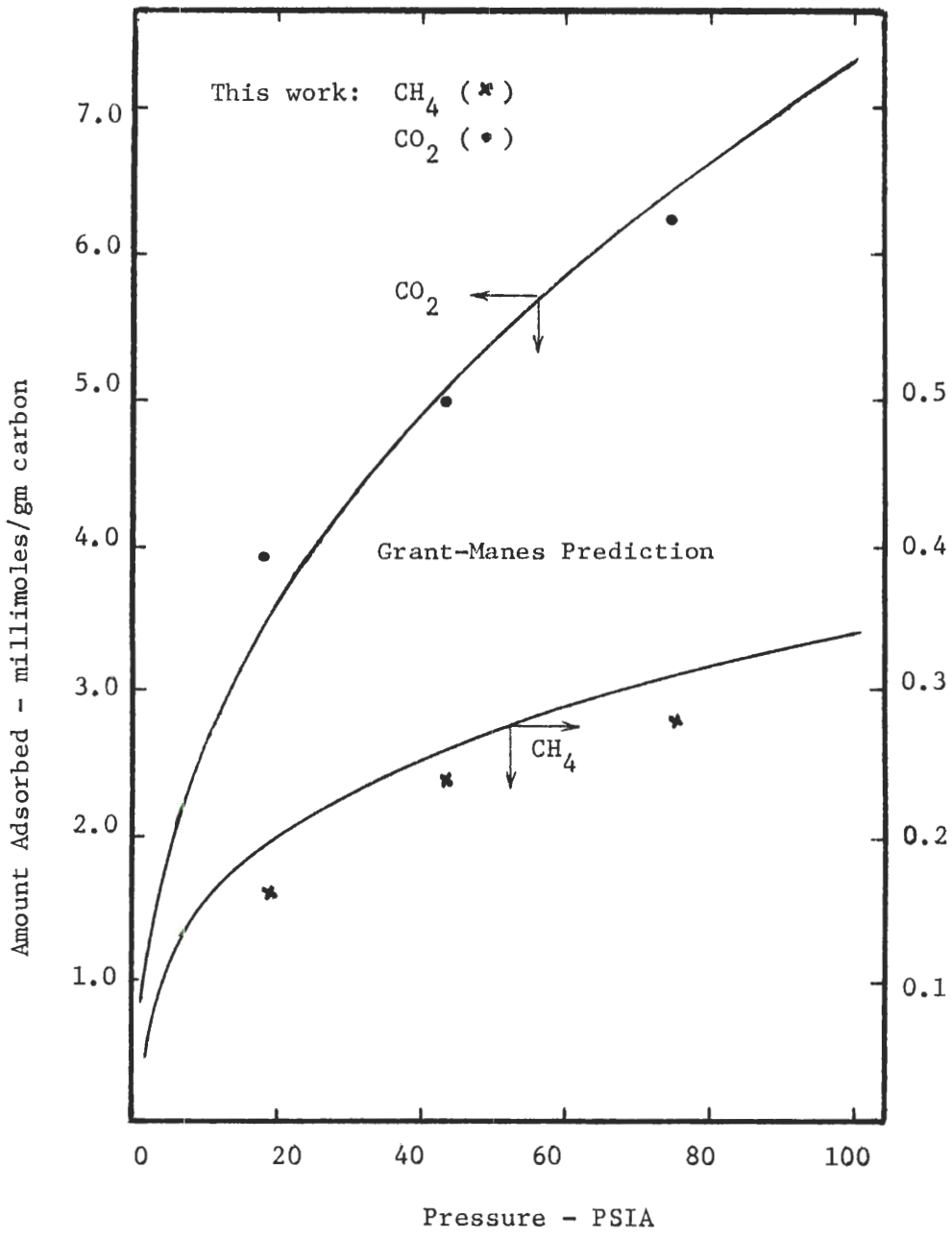

Figure 12. Methane (18.8 Mole %) - Carbon Dioxide (81.2 Mole %) Isotherm at 260.2 K.

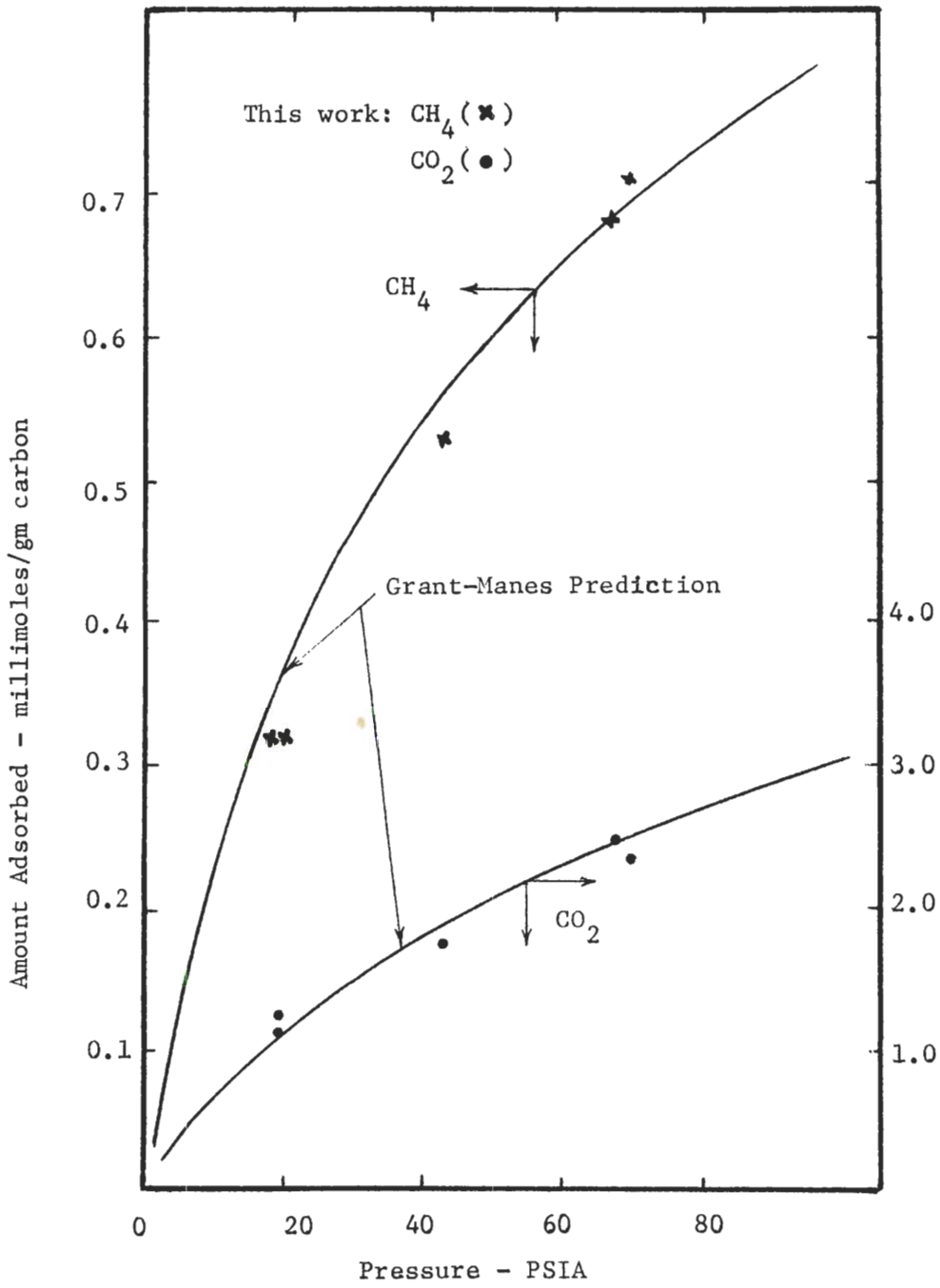

Figure 13. Methane (49.8 Mole %) - Carbon Dioxide (50.2 Mole %) Isotherm at 301.4 K.

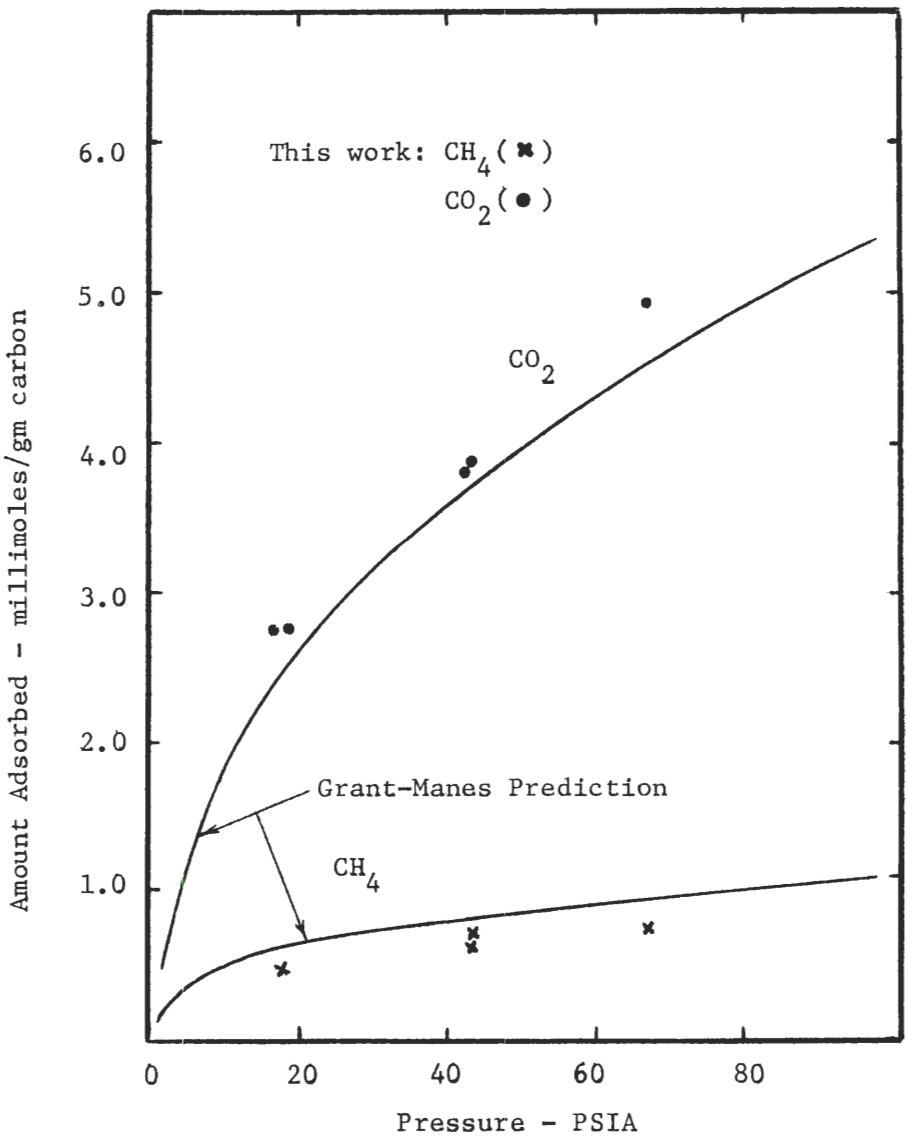

Figure 14. Methane (49.8 Mole %) - Carbon Dioxide (50.2 Mole %) Isotherms at 260.2 K.

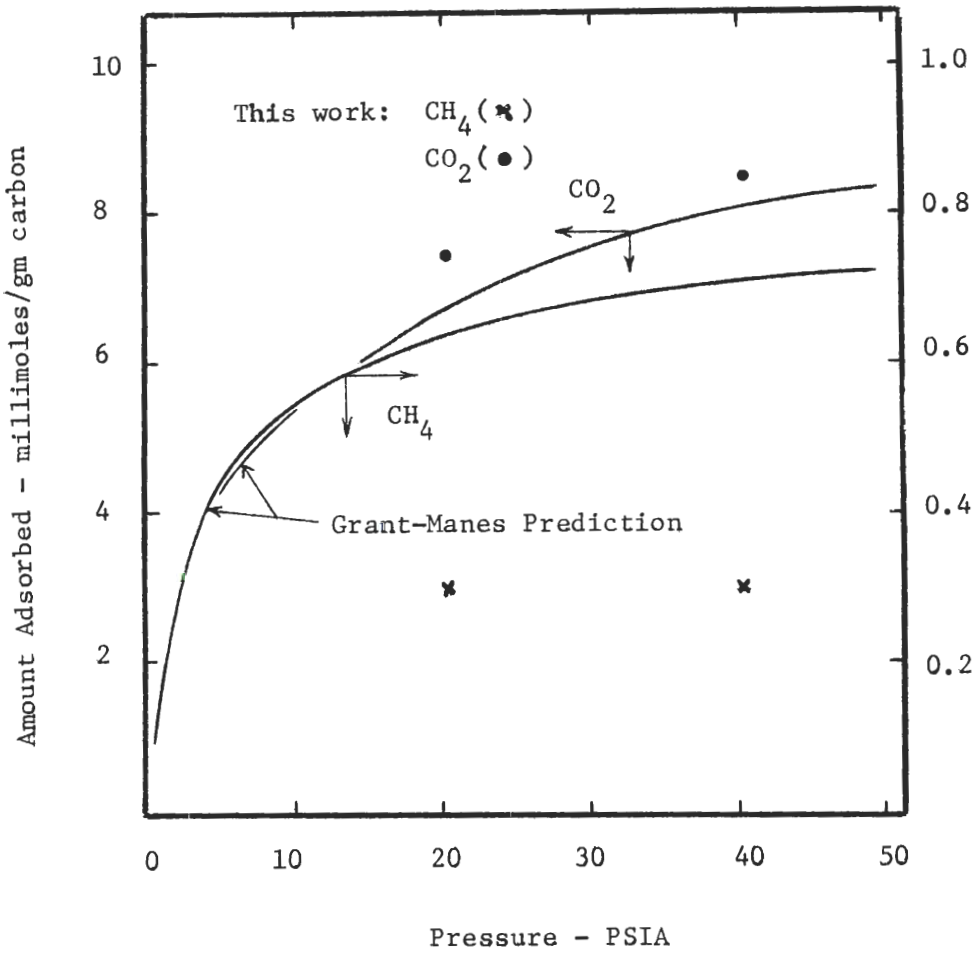

Figure 15. Methane (49.8 Mole %) - Carbon Dioxide (50.2 Mole %) Isotherm at 212.7 K.

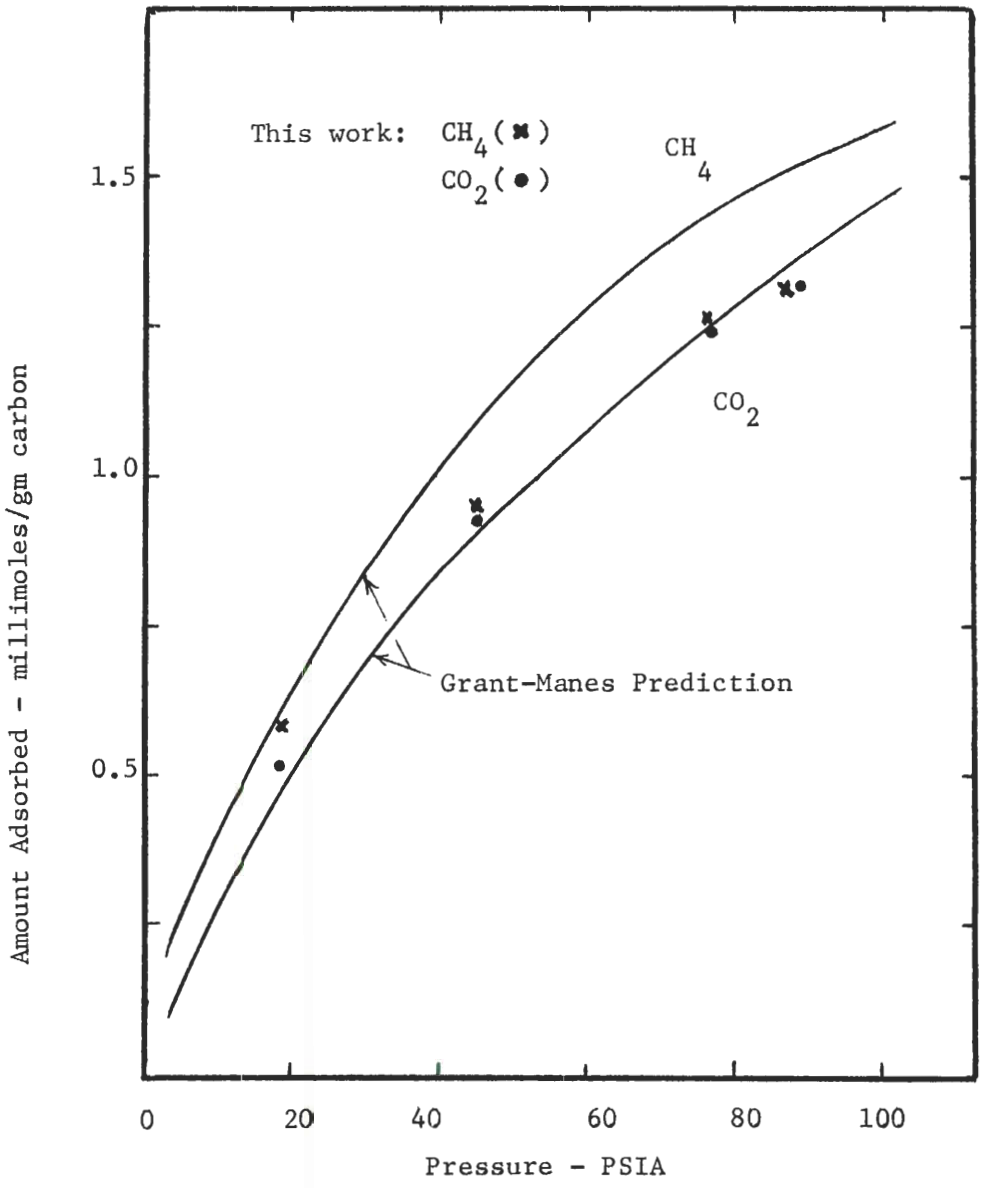

Figure 16. Methane (79.5 Mole %) - Carbon Dioxide (20.5 Mole %) Isotherm at 301.4 K.

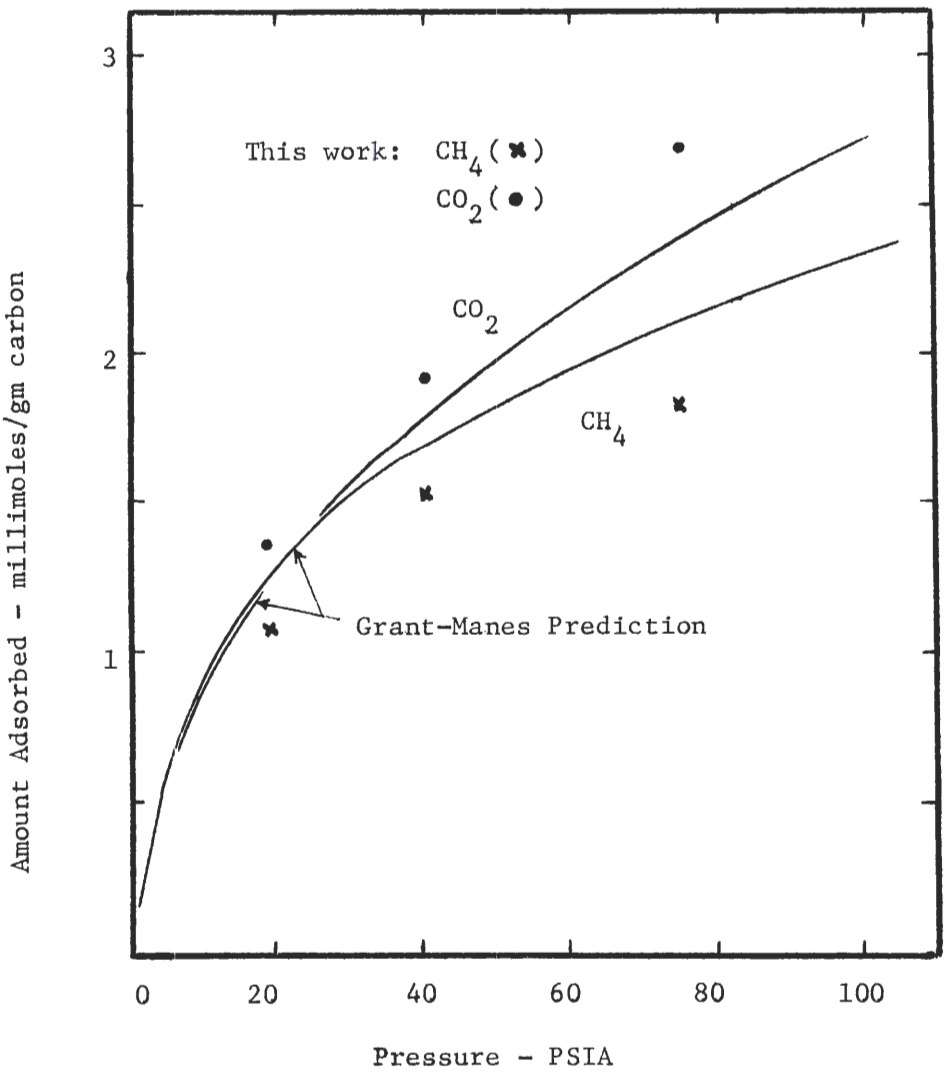

Figure 17. Methane (79.5 Mole %) - Carbon Dioxide (20.5 Mole %) Isotherm at 260.2 K.

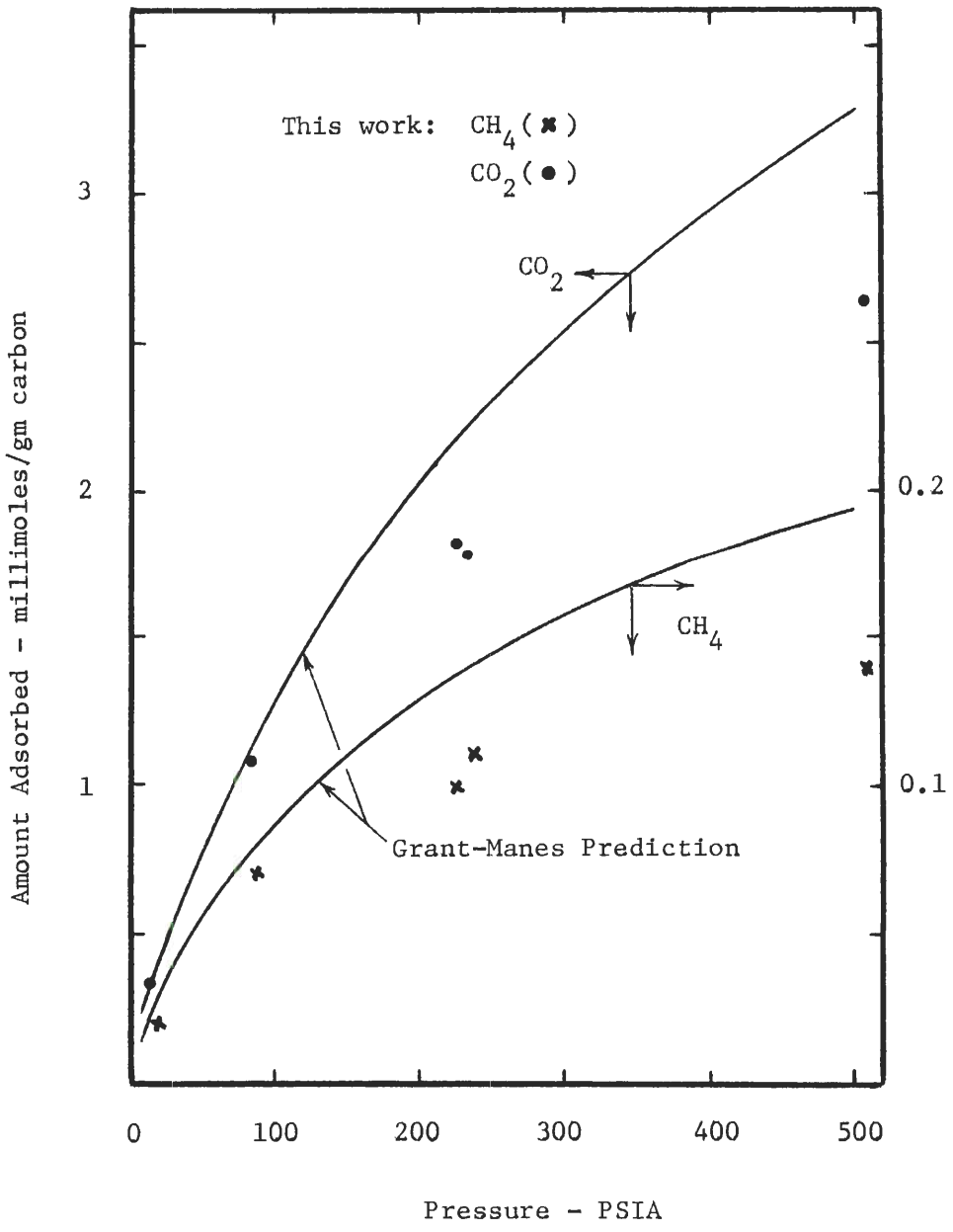

Figure 18. Methane (2.07 Mole %) - Carbon Dioxide (9.77 Mole %) - Hydrogen (88.2 Mole %) Isotherm at 301.4 K.

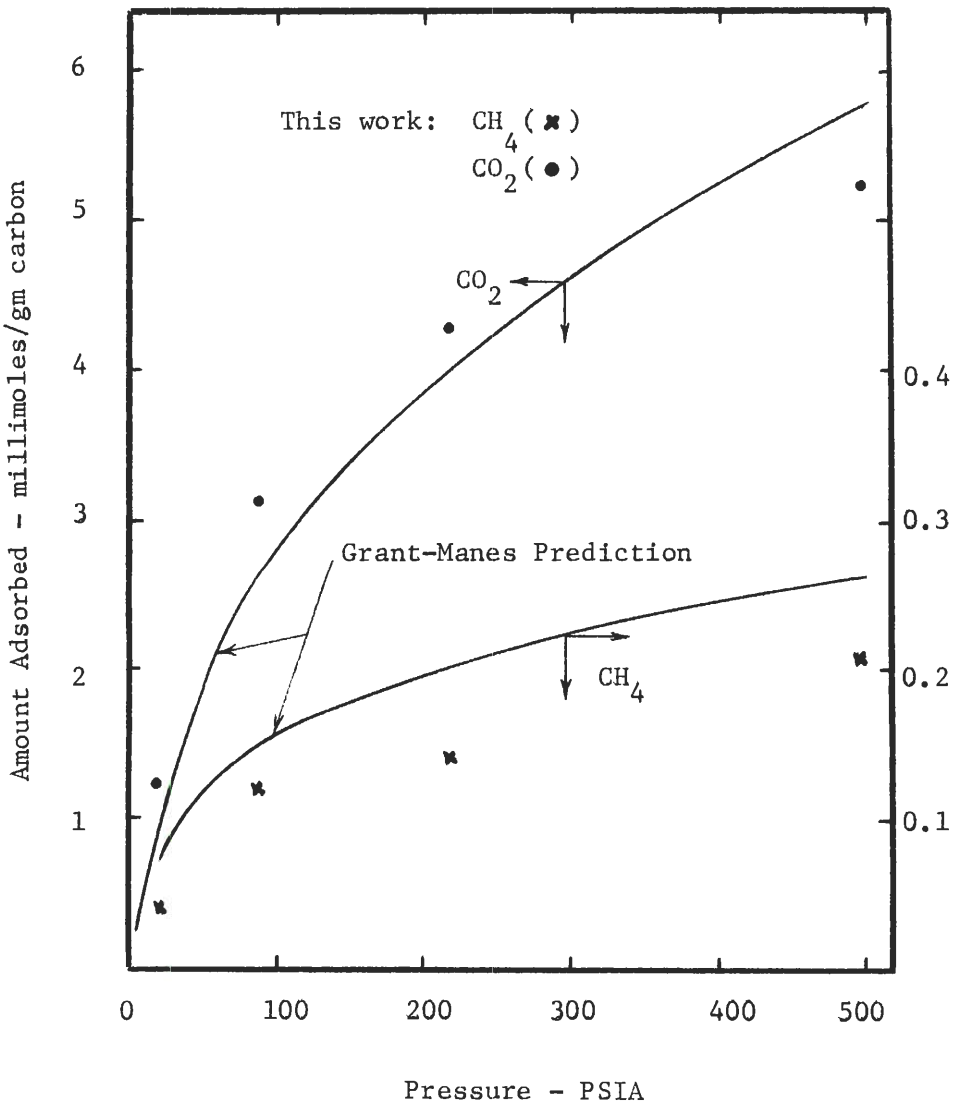

Figure 19. Methane (2.07 Mole %) - Carbon Dioxide (9.77 Mole %) - Hydrogen (88.2 Mole %) Isotherm at 260.2 K.

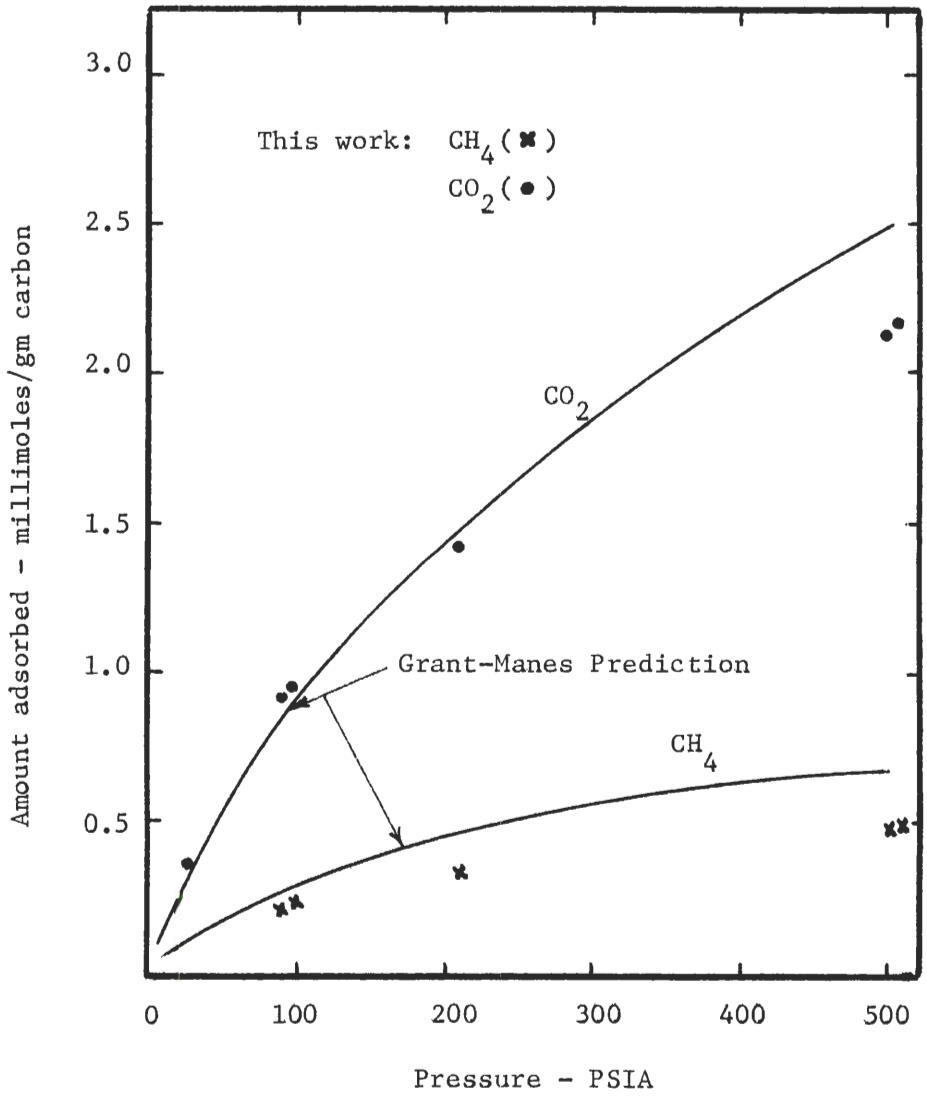

Figure 20. Methane (6.60 Mole %) - Carbon Dioxide (6.96 Mole %) - Hydrogen (86.4 Mole %) Isotherm at 301.4 K.

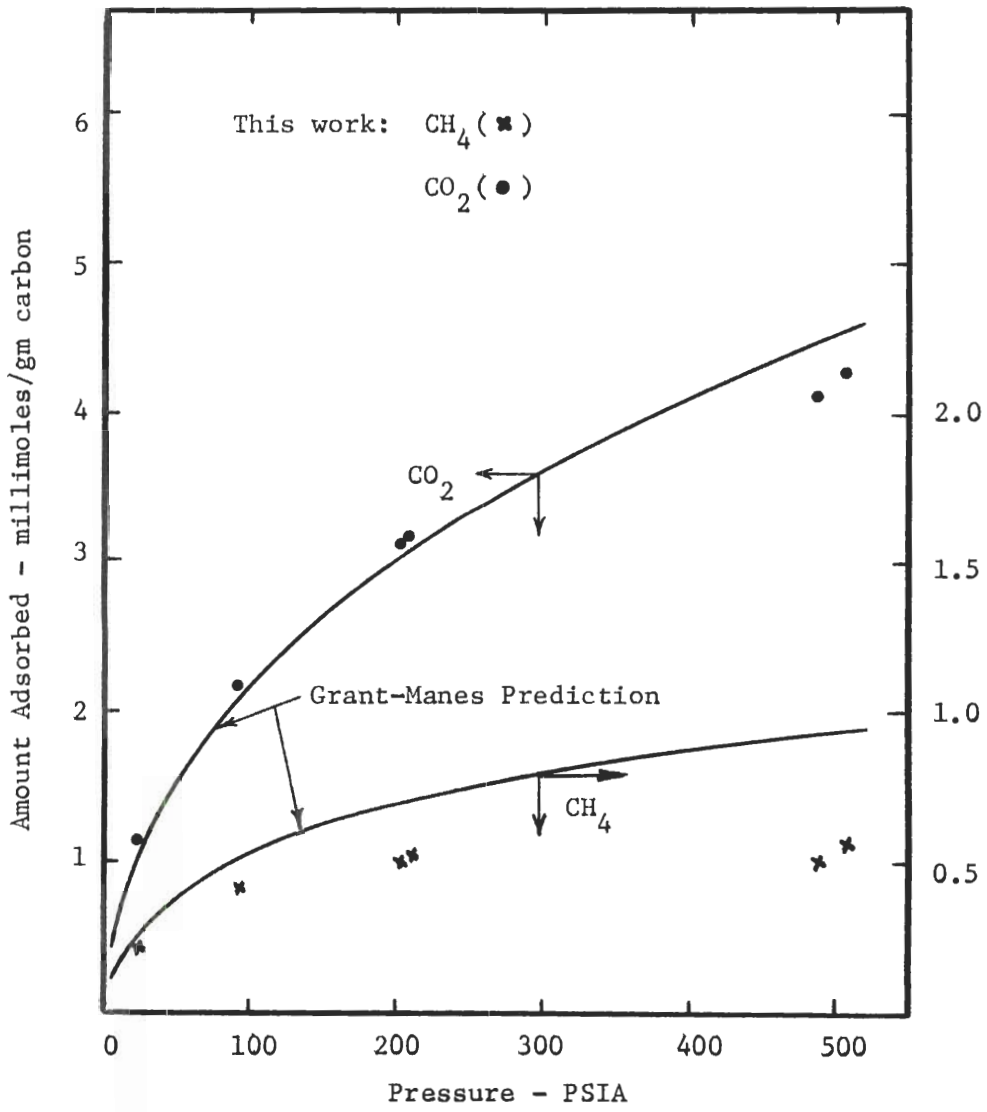

Figure 21. Methane (6.60 Mole %) - Carbon Dioxide (6.95 Mole %) - Hydrogen (86.4 Mole %) Isotherm at 260.2 K.

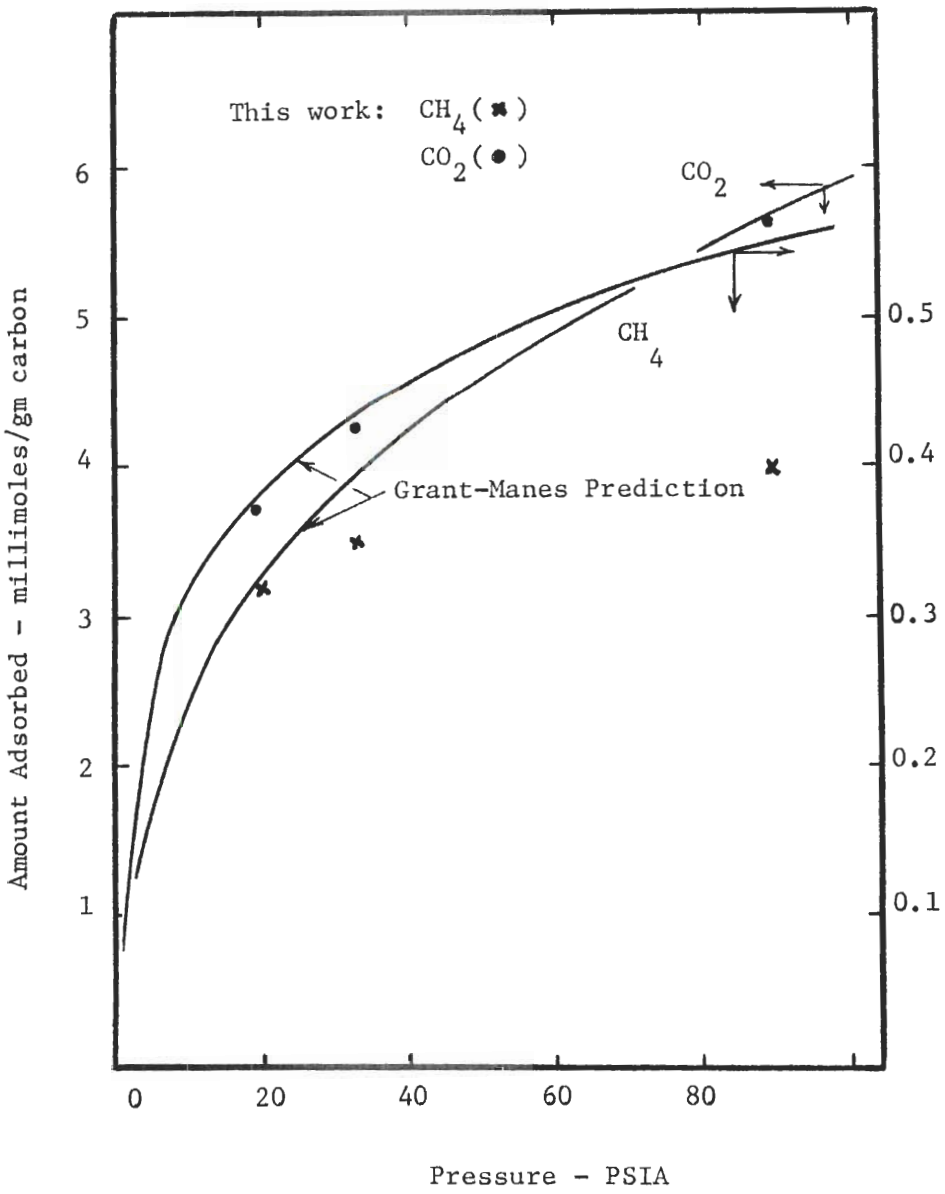

Figure 22. Methane (6.60 Mole %) - Carbon Dioxide (6.95 Mole %) - Hydrogen (86.4 Mole %) Isotherm at 212.7 K.

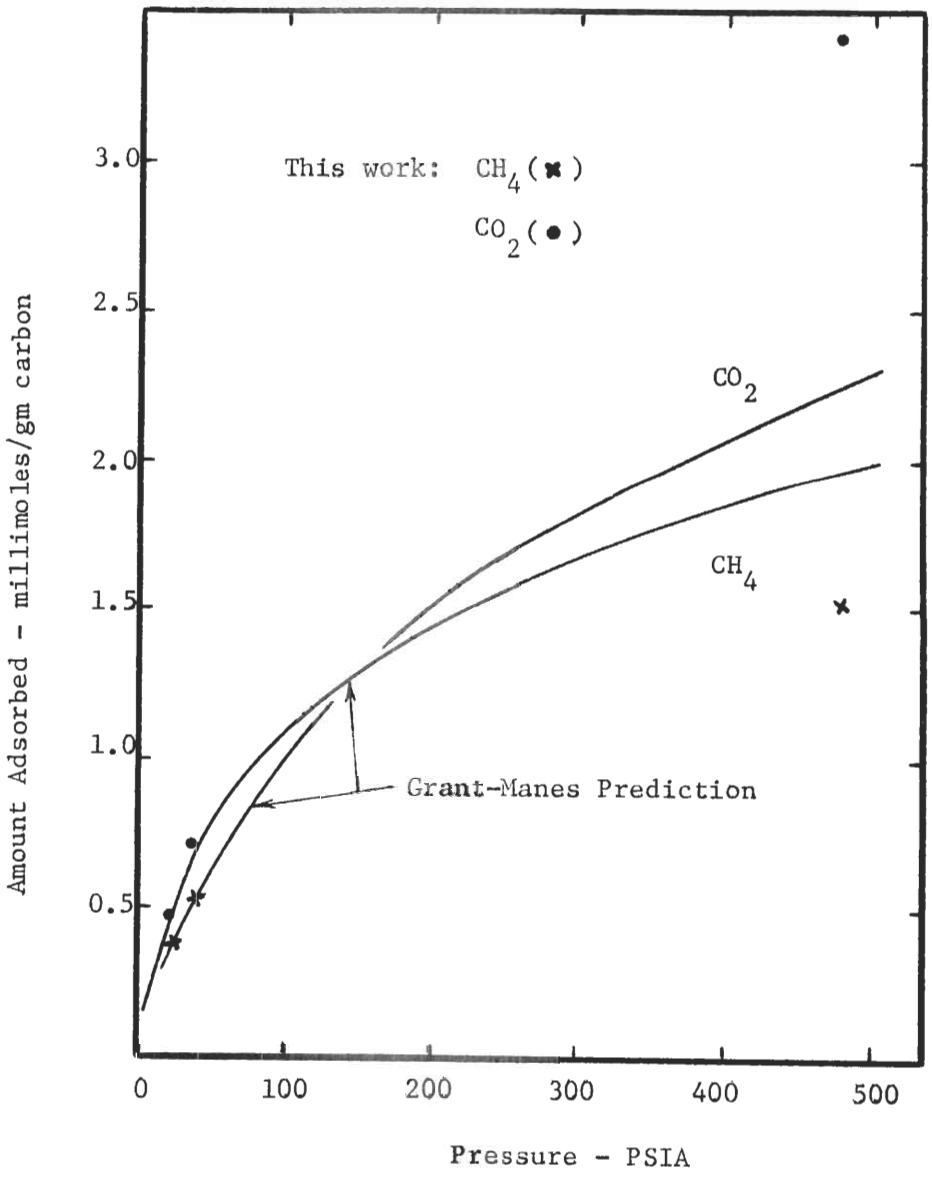

Figure 23. Methane (10.8 Mole %) - Carbon Dioxide (2.86 Mole %) - Hydrogen (86.3 Mole %) Isotherm at 260.2 K.

the various mixtures, plots were made of ln N and $(\ln Ps/P)^2/T^2$ for each of the data sets. Each mixture was drawn on a separate plot with the individual isotherms identified. For certain of the isotherms, excellent straight line relations were found. However, an inspection of the entire set of mixture plots indicated that the slopes of the best-fit lines were temperature dependent in many cases. This finding coupled with the conclusion discussed earlier in this chapter for the pure methane and carbon dioxide isotherms was the reason for not pursuing this approach further. It was concluded that more development and data would be required before the D-R equation could be applied in a general way to mixtures where the partial pressure of the components exceeds one atmosphere or where the temperature is above the critical of the components. Another shortcoming of the mixture method proposed by Bering et al.[5] is the failure of equation (IV-20) to predict accurately adsorbate composition for many systems. However, the adsorbate composition prediction results shown in Tables 12 and 13 in Appendix E show that equation (IV-10) would be satisfactory for this part of the problem.

Another method examined was use of the Langmuir mixture isotherm which is

$$N_i = \frac{N_i^* b_i P_i}{1 + b_1 P_1 + b_2 P_2} \qquad \text{(V-1)}$$

Equation (V-1) could be used for both the binary and ternary gas mixtures because the adsorbate was a binary for either case. Ideally, the values for b_i solved from each of the pure isotherms would serve for the constants were then solved for the mixture isotherms at high pressures. In this case, equation (V-1) did not give a good representation for the

lower pressure region. No further attempts were made to use the Langmuir equation.

Relative Volatility

A quantity defined and carried over from distillation technology was used by Lewis et al.[28] in their adsorption studies on mixtures. This variable is called the selectivity or relative volatility and is defined by

$$\alpha = \frac{X_2 Y_1}{X_1 Y_2} \tag{V-2}$$

Application of this variable is limited to binary adsorbates.

The relative volatility has a simple meaning with a mixed adsorbate for which Raoult's law applies

$$X_i Ps_i = Y_i P \tag{V-3}$$

A definition for an ideal system could be one in which equation (V-3) would hold for both components. Dividing the two equations (V-3) expressed in terms of the individual components gives

$$\frac{X_2 Y_1}{X_1 Y_2} = \frac{Ps_1}{Ps_2} \tag{V-4}$$

which is seen to be the definition of the relative volatility. But since the adsorption system is isothermal, the component vapor pressures must be constant. Thus equation (V-4) indicates that an ideal system will have a relative volatility for two given components which will be constant regardless of the gas phase composition. Values for α have been computed and are presented in Appendix E in Table 9 for the binaries

and in Table 10 for the ternaries studied. The fact that these values are not constant shows that the system does not conform to the above definition of ideality. Lewis et al.[28] found that α was a useful quantity for correlating adsorption from certain binary hydrocarbon mixtures.

Adsorption Enhancement Factor

Working only with the pure component isotherms and the physical properties for mixture systems, there are many quantities which may be defined with a sound basis in thermodynamics. One such quantity which has been studied by Hiza and Kidnay[23,24] is called the adsorption enhancement factor defined as

$$\phi_A = \frac{Y_i P}{P^o(N_i, T)} \qquad \text{(V-5)}$$

This variable is the ratio of component partial pressure to the pure isotherm pressure, P^o, for an equal amount adsorbed. The adsorption enhancement factor has a foundation in theory. It arises when the adsorption mechanism for pure gases and for mixtures is related via the chemical potential. The work by Hiza and Kidnay[24] indicated several useful conclusions for ϕ_A in the domain studied. ϕ_A was shown to increase monotonously with pressure and have limiting values of one at low pressure. Their work also showed that the values for ϕ_A were independent of the type of adsorbent. This conclusion was based on experiments with three different generic classes of adsorbent. It was anticipated by Kidnay et al.[25] that the correlation of adsorption enhancement factor would be different for a mixed adsorbate due to the more complex interaction relations in both the gas and adsorbed phases.

The methane and carbon dioxide adsorption enhancement factors were calculated for the mixture experimental points of this study. These values are reported in Appendix E in Tables 10 and 11. It should be noted that these values have a significant possible error due to the quantity in the denominator of the definition. The pressure determined from the pure isotherm is subject to the uncertainties of the mixture isotherm value and the pure isotherm. This uncertainty is greatest in the low pressure range where the ϕ_A concept would find less use. The calculated uncertainty for the adsorption enhancement factor at higher pressures is ± 13 per cent. The limited conclusions which may be drawn from this study on the adsorption enhancement factor are presented in Chapter VI.

CHAPTER VI

CONCLUSIONS

The experimental data obtained in this study were used to show that an Adsorption Potential Theory characteristic curve may be used to represent the adsorption of different substances over a wide pressure range and several temperatures. Mixture results were used to show further that these data can be used to define a characteristic curve which coincides with that constructed from the pure compounds. In particular, it was shown that for the pressure-temperature domain of this study, the Grant and Manes[21] method of predicting adsorption from gas mixtures (using the Adsorption Potential Theory with the saturated liquid at the normal boiling point for the adsorbate molar volume) gave good results.

Subject to the limited available experimental evidence, it should be stated that the effectiveness of the Grant and Manes method in predicting the experimental results of this study and the success of others with the Adsorption Potential Theory, is considered to be a general support of that method and not merely a technique limited to prediction of adsorption of methane and carbon dioxide on activated carbon. Lewis *et al.*[27] showed that the C1 to C4 hydrocarbons could be correlated on single characteristic curves for carbon and silica gel adsorbents at a single temperature with slightly different curves for saturated and unsaturated hydrocarbons in the low pressure region. Grant and Manes[20] extended that result to show that methane, argon, nitrogen and other hydrocarbons throuch C5 could be characterized on a single curve for the

same carbon used in this study using data both above and below component critical temperatures. Hasz and Barrere[22] showed that a single curve would characterize carbon dioxide and C1 through C4 paraffin hydrocarbons on activated carbon at one temperature with the use of an empirical molar volume technique for the adsorbates. This study has used pure methane and carbon dioxide isotherms at three different temperatures and a range of pressures to construct a single characteristic curve. It is expected that this curve could be used to predict adsorption of other components on the same carbon with the use of a suitable molar volume relation.

Because of the limited amount of experimental work which has been published to date on adsorption from gas mixtures, the following limitations must be imposed on the conclusion that the Grant-Manes method as described above is the best mixture adsorption prediction technique:

1. Total pressure limited to 100 PSIA.
2. An essentially binary adsorbate for either binary or ternary gas mixtures.
3. A sorption process limited to physical adsorption.

For the domain where the method works well, it was found that pressure is as satisfactory as fugacity for the variable. This is because pressure and fugacity are essentially equal in the region below 100 PSIA for the system studied. For the pressure domain above that where the method works well, the following observations were made:

1. The lesser adsorbed component is over predicted except for the case where the greater adsorbed component is a high proportion of the gas phase.

2. The greater adsorbed component is under predicted.
3. The equi-potential concept for mixtures, equation (IV-10), as expressed by Grant-Manes works well to predict adsorbate composition.
4. The Lewis empirical relation for adsorbate composition gives more accurate results for higher total pressures but is still inferior to the equi-potential prediction.

Because of the very limited nature of the data in this study and the lack of extensive low temperature and high pressure experiments with adsorption from gas mixtures from other sources, there is a severe limitation on the certainty of conclusions which may be drawn with regard to the adsorption enhancement factor. Subject to the limitations of the system in this study, the following may be said about this variable for both binary and ternary gas mixtures:

1. ϕ_A always increases with pressure.
2. The greater adsorbed component always has the smaller ϕ_A values.
3. ϕ_A increases with decreasing temperature except for the case where the lesser adsorbed component critical temperature is approached.
4. ϕ_A generally increases with decreasing composition.
5. The value for ϕ_A may not approach one for binary adsorbates at low pressures.

It is thought that the adsorption enhancement factor could be a useful tool in adsorption prediction for high pressures and for the lesser adsorbed component. It is this region where the Grant-Manes method has significant errors. In the present stage, the adsorption

enhancement factor is only useful as an interpolation tool. Considerable additional study will be required before general techniques can be developed for this variable.

CHAPTER VII

RECOMMENDATIONS

For future studies of adsorption from gas mixtures it would be useful to consider the following:

1. Determine adsorption results from a system similar to that used in this study with the exception that another component with a critical temperature above room temperature should be substituted for carbon dioxide to learn further about the accuracy of the Grant-Manes method.

2. Another study similar to this one except that a component with a critical temperature below 250 K should be substituted for the carbon dioxide. The amount of experimental data covering such a system at pressures and temperatures above and below the critical are very scarce.

3. Much useful information could be derived from the study of a mixture which gave a ternary adsorbate. It would be helpful to verify if the equi-potential concept holds.

4. Variation of the pseudo-saturated pressure as an input parameter to improve the correlation could be useful in indicating if a general method could be developed.

5. Further study and application of the Dubinin-Radushkevich relation to mixtures should be useful as it appears that this function might lead to good predictions for the total amount of adsorbate. The

equi-potential technique should serve as a satisfactory method for the prediction of adsorbate composition. Thus the adsorption problem might be solved without the need for construction of characteristic curves.

APPENDICES

APPENDIX A

APPARATUS DETAILS

Most of the major components of the adsorption system are located within the cryostat. This portion of the system is shown schematically in Figure 24. The adsorbent vessel was made from pure copper rod with a blind flange closure of the same material. The vessel is a right cylinder 2.0 inches outside diameter and 4.30 inches long with an internal diameter of 1.5 inches. The internal volume is approximately 70 cc. The closure flange is the same diameter and 0.75 inches thick with a raised face for a confined gasket of Teflon, approximately 1/16 inch thick and 1/8 inch wide. This flange is held in place with eight 8-32 machine screws of Series 300 stainless steel secured into blind tapped holes in an integral ring that is part of the vessel wall. The flange was designed for a maximum working pressure of 100 atmospheres but was only tested to 1,100 PSIG with hydrogen gas. The flange closure is the limiting element on maximum temperature and pressure for the adsorption system.

There are two tubing connections to the adsorption vessel. These are each 1/8 inch outside diameter, 0.035 inch wall, copper tubing silver soldered in place. Flow into the cell is from the top. The carbon is held in place by brass screens and a small quantity of glass wool. The amount of 20/60 mesh Pittsburgh Type BPL carbon loaded into the adsorption cell was 35.38 grams. From the adsorption cell, the gas goes to the heat exchanger described below and then to a wet test meter. The exchanger

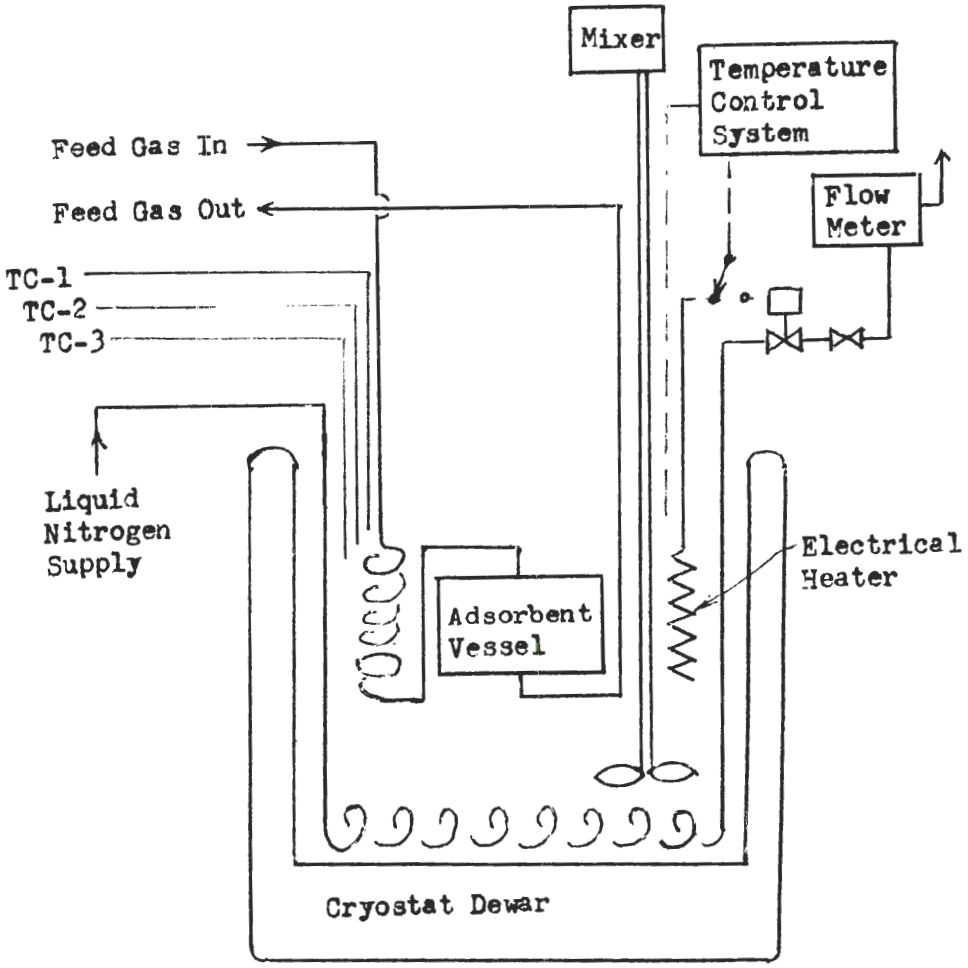

Figure 24. Schematic Adsorbent Vessel Cryostat

and connecting tubing are not part of the adsorption dead space.

All valves used on the apparatus are Whitey Type IRF brass body needle valves. Swagelok fittings were used where mechanical joints were required. Silver solder joints were used wherever possible on the apparatus and silver or soft solder joints with several rubber or plastic tubing connections were used on the vacuum system.

All tubing used for the apparatus was copper with the exception of some stainless steel or monel used to reduce heat leak into the cryostat.

The cryostat is a cylindrical glass Dewar vessel 13.5 by 70 cm with either water or hexane used as the bath fluid depending upon the temperature of the experiment. The adsorption cell was always at least 25 cm below the level of the cryostat fluid during experiments.

In addition to the adsorption vessel and connecting tubing, the cryostat contains a copper coil of 1/4 inch outside diameter tubing for the circulation of the liquid nitrogen used as a cryostat refrigerant, an electrical heating element, a mechanical mixer, two glass thermowells containing Chromel-Constantan reference thermocouples, one bare thermocouple and a double junction control thermocouple of the same wires. All of these enter the Dewar from the top. The Dewar was raised into position for each experimental run and lowered to accomplish the desorption.

Pressure within the adsorption cell was measured by either a mercury-in-glass manometer or a medium or high range Bourdon type test quality pressure gauge. All three units are permanently mounted on the apparatus and which unit is used for an experiment depends upon the

pressure level. The correction curves for medium pressure gauge P1 and high pressure gauge P2 are presented as Figures 25 and 26.

Pressure of the feed gas is controlled by a gas dome type pressure regulator known commercially as the "Phoenix" style made by the Hoke Company. The supply gas passes through a double tube type heat exchanger which exchanges heat in counterflow with the effluent gas from the adsorption cell during mixture experiments. The chief purpose of the exchanger was to bring the gas closer to cryostat temperature to improve bath temperature control. From the heat exchanger, the gas enters the cryostat and passes through a copper coil of 1/8 inch O. D. tubing 200 cm long to insure it has reached cryostat temperature before entering the adsorption cell.

The liquid nitrogen refrigerant was supplied to the apparatus from a metal Dewar vessel which was pressurized sufficiently to cause flow through the cryostat cooling coil.

The sample reservoir shown in Figure 2 in Chapter II consists of a 2 liter Pyrex filter flask fitted with an internal mixer fabricated from monel tubing, brass bearings, brass shim stock impellers, and a magnetic mixer drive system. The sample reservoir was fully immersed in a water bath supplied with a continuously circulating flow from a commercial water thermostat. The mixer drive was outside and below the water bath. The same water bath contained the gas reservoir which was a lecture size steel gas cylinder with an internal volume of approximately 800 cc. Pressure measurement in the sample reservoir was by mercury manometer. The gas reservoir has a mercury manometer and the Heise pressure gauge.

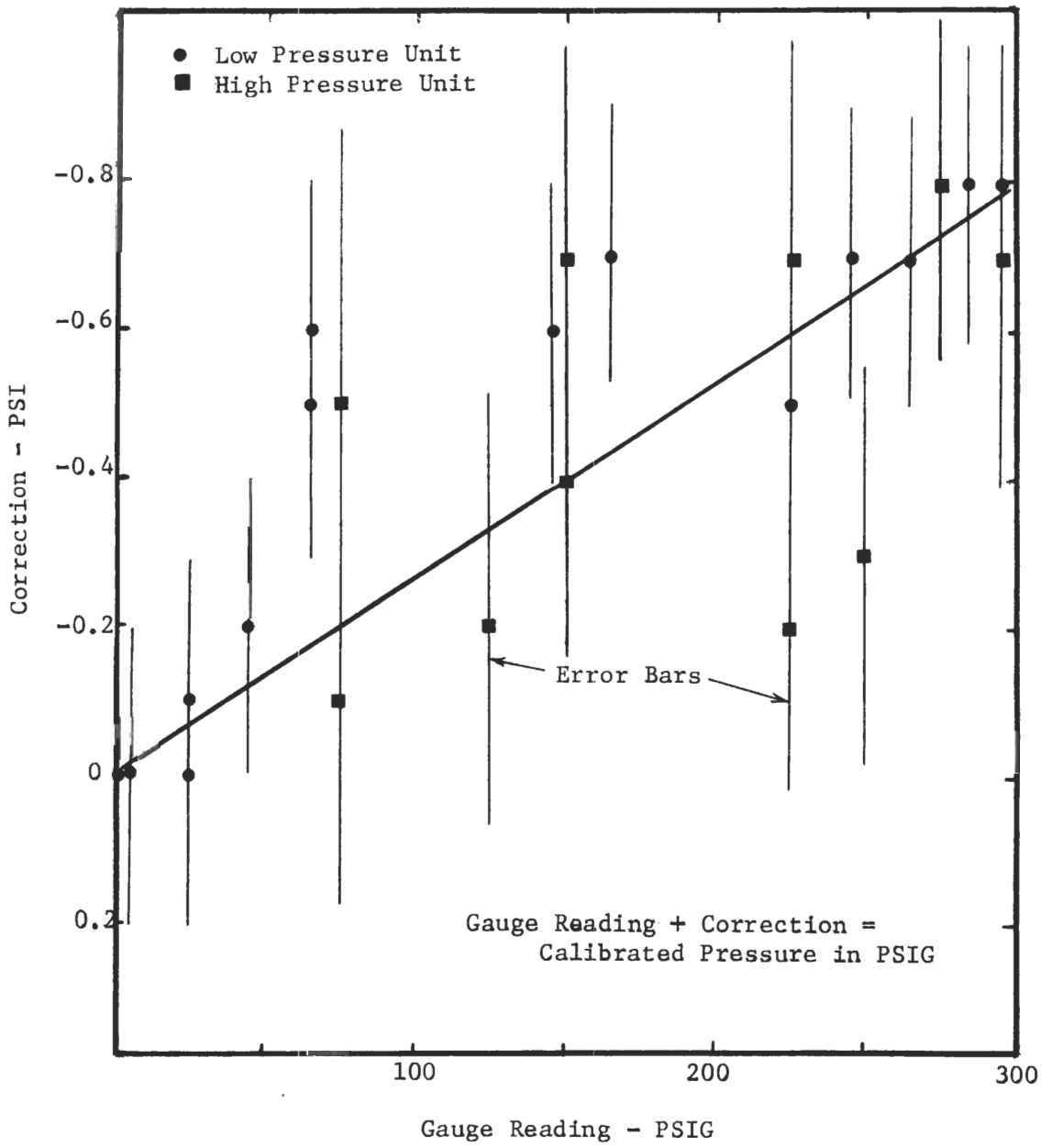

Figure 25. Correction Curve for Pressure Gauge P1

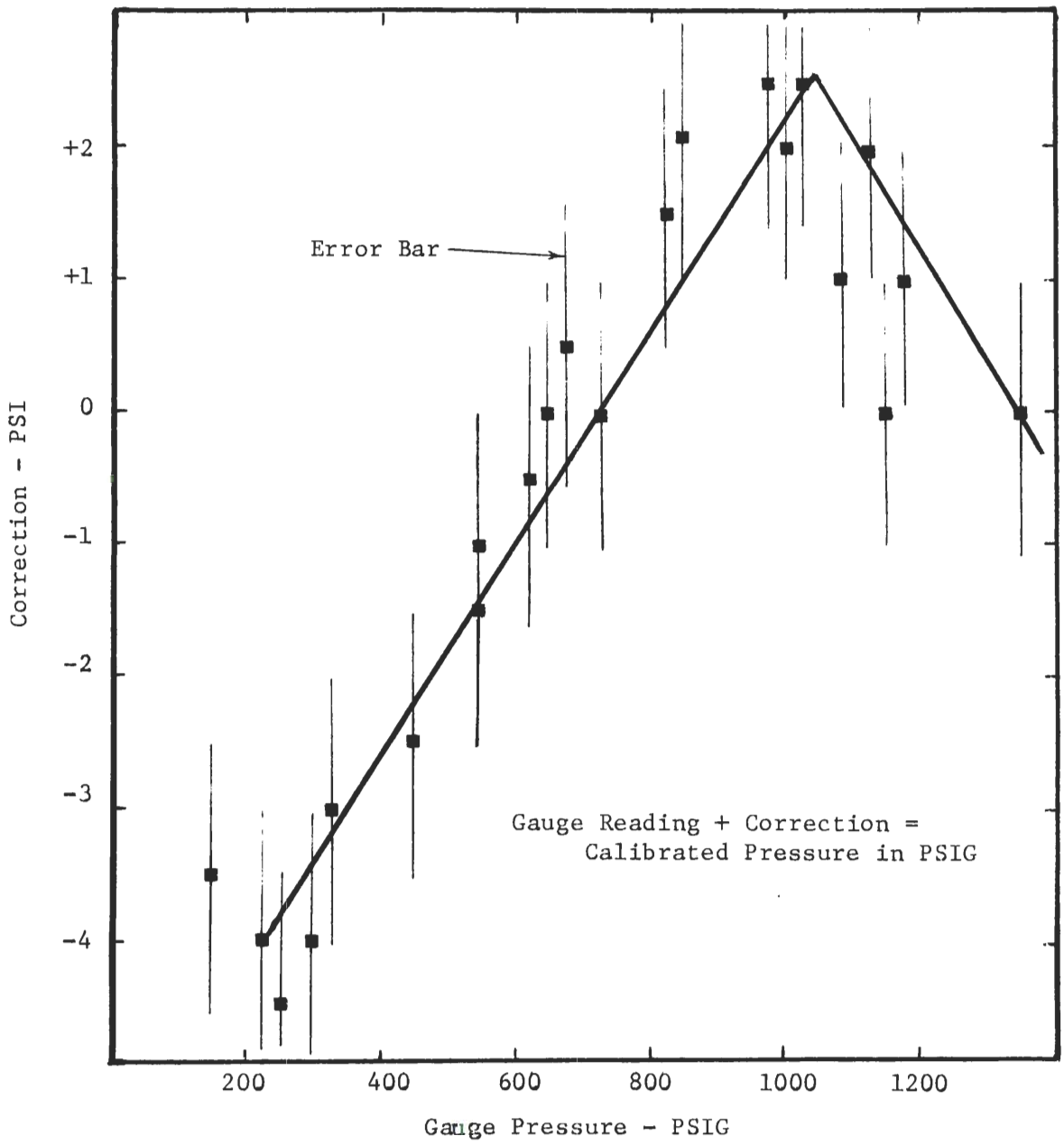

Figure 26. Correction Curve for Pressure Gauge P2

APPENDIX B

THERMOCOUPLE CALIBRATION

Upon completion of the original adsorption apparatus, there were five Type E, Chromel-Constantan thermocouples within the cryostat. All of these thermocouples were made by soft soldering 30 BWG nylon insulated wire which had been purchased for the laboratory many years previously. The Constantan was Advance made by the Driver-Harris Company with a resistance of 3.0 ohms/foot. The Chromel wire was Type T-1 (121 Alloy) also made by Driver Harris.

Two of the thermocouples were installed in individual glass wells made from 7 mm tubing and 5 to 8 cm of hexane was kept in these wells to improve thermal transfer. Only the two thermocouples in glass wells were calibrated using a capsule type platinum resistance thermometer, Leeds and Northrup Serial 1583526 and the potentiometer components described in Chapter II.

All of the calibration work was accomplished within the cryostat. The effect of changing resistance thermometer current was studied. The reference ice bath was agitated during several experiments to be certain there was no thermal stratification. Measurements were also taken with another platinum resistance thermometer which had been calibrated by the National Bureau of Standards years previously. This was a long glass enclosed unit inserted into the cryostat from the top. It was decided to use the capsule-type thermometer as the primary standard as it appeared to give the most stable readings in service and the National

Bureau of Standards calibration had been performed more recently.

The potentiometer system described in Chapter II was used to read EMF values from the resistance thermometer, standard resistor, and the two thermocouples being calibrated. The thermometer EMF and the standard cell EMF were sufficient, with the use of the resistance thermometer equation which gave the temperature as a function of electrical resistance, to allow the indicated temperature to be calculated. All significant figures read on the potentiometer were used as input to a computer program which printed the thermometer resistance to six figures. This value was then used with a printout of the thermometer resistance with temperature at 0.1 K intervals and a desk calculator to linearly interpolate and thus to establish the indicated temperature to the nearest 0.01 K.

The indicated temperature was plotted as a function of time and the two thermocouple EMF values were shown on the same plot. This plot was used to determine equilibrium EMF as a function of temperature for each of the thermocouples. Four to ten pairs of values were determined at each temperature level at increments of approximately 10 K degrees for the range from 200 to 310 K. All of the values for each thermocouple were used as inputs to a least square polynomial fitting program to obtain the best fitting function and learn the deviations of all of the experimental values from the smooth function. When it was found that a fit which gave deviations less than 0.1 K degree could not be obtained, it was decided to calibrate at the three particular temperatures used for all of the adsorption experiments. This was done with the control system in operation holding the cryostat at each temperature for from one to several hours until it was deemed that satisfactory equilibrium

values had been obtained. It was apparent that thermal stratification within the Dewar was severe at the beginning of each run and the mixer was required to be in service whenever the cryostat was used.

All temperatures are reported on a Kelvin Scale using t in degrees centigrade on the International Temperature Scale of 1948.

$$T\ (K) = t\ (^{\circ}C) + 273.15 \qquad \text{(B-1)}$$

The resistance thermometer used was calibrated by the National Bureau of Standards in Test No. 3.1/G-29918 completed January 9, 1962. The two calibrated thermocouples were found to have EMF values which were essentially the same at each of the three calibrated temperatures. With an ice reference bath, the EMF values at 212.7, 260.2, and 301.4 K were 3.169, 0.715, and -1.604 millivolt, respectively. The potentiometer system was used over a period of approximately one year and recalibrated at the beginning and end of this period. The measurement accuracy of the system is believed to be within two microvolts.

APPENDIX C

GAS CHROMATOGRAPH CALIBRATION

A LOENCO, Model 2400-T1, Serial 1014, chromatograph was used with a PERKIN-ELMER gas sampling valve with the 5.0 cc loop installed. The column was activated by flowing pure helium for one hour at 200°C. Output from the gas chromatograph was recorded on a Leeds and Northrup Model W potentiometer with a 2.0 millivolt span and a two inch per minute chart speed. Chromatograph operating conditions are shown in Table 4.

Table 4. Gas Chromatograph Operating Conditions

Column:	1/4 inch outside diameter stainless steel tubing 80 cm long filled with 40/80 mesh Silica Gel
Carrier Gas:	Helium; flow rate = 38.2 cc/minute at 50 PSIG inlet reference rate = 19.8 cc/minute
Thermal conductivity cell filament current = 69.5 milliamperes	
Column, injector and detector temperatures = 60°C	
Time required for peak:	Methane = 1½ minutes Carbon Dioxide = 6 minutes

Experimental work with several columns showed that it was practical to analyze the methane and carbon dioxide on the same instrument. The basic problem was to find a single column which would separate these two

components from a binary or a ternary mixture with hydrogen. As seen from the peak times in Table 4, the conditions used gave a satisfactory result. Experiments were performed with the operating conditions to find the combinations which would give distinct peak heights linearly proportional to composition. The conditions shown were selected after varying the column, carrier gas rate, operating temperature, detector cell current, sample size and silica gel particle size.

It was necessary to calibrate the chromatograph over the full range from 0 to 100 per cent to handle all anticipated samples from the mixture experiments. The calibration was performed with the use of known mixtures prepared with a sample mixing buret which had been designed and built by Kirk.[26] This apparatus was used to prepare methane-hydrogen and carbon dioxide-hydrogen binary mixtures. Gas imperfection corrections were found to be unnecessary for these mixtures.

To allow for the many day-to-day fluctuations which can affect a chromatograph calibration, a series of reference cylinders containing ternary mixtures of the same gases for the full range of attenuation switch settings was prepared. Samples of these reference gases were checked frequently throughout the calibration experiments. On subsequent days, these reference gases were checked and used to provide a single correction factor for the following possible causes of calibration shift for the gas chromatograph:

1. Variation in atmospheric pressure.
2. Room temperature variation.
3. Temperature variations within the chromatograph.
4. Carrier gas fluctuations.

5. Voltage and recorder changes.

6. Detector system changes.

The results from all of the calibration experiments were plotted for each of the gases for each attenuation switch setting from "2X" to the setting required for a 100 per cent sample. Best fit straight lines were drawn on all of these plots. These plots were used to determine compositions from the experimental peak heights. Using pure methane and pure carbon dioxide as references gases gave a good check whenever analyses were made for high compositions of these components. The reference gases were from the same sources as the feed gas mixtures.

A correlating plot was made for each gas with the experimental calibration points which covered the full range of samples tested. This correlating curve is a semi-log plot of peak height times attenuation switch setting as the abscissa with the same variable divided by composition expressed as per cent as the ordinate. A band representing plus and minus three per cent accuracy was added to the correlating curve. It is believed that the accuracy of all analyses accomplished during the experiments falls within this accuracy range. The correlating curve for carbon dioxide is presented as Figure 27 and the curve for methane is Figure 28.

The same method of analysis by peak height using reference mixtures for standardization has been used by Kirk,[26] Garber,[16] and Yoon,[41] and others in this laboratory. An additional calibration was performed several months after the original work. There was an indirect calibration check during the binary adsorption experiments when binary samples of methane and carbon dioxide were obtained on desorption. The

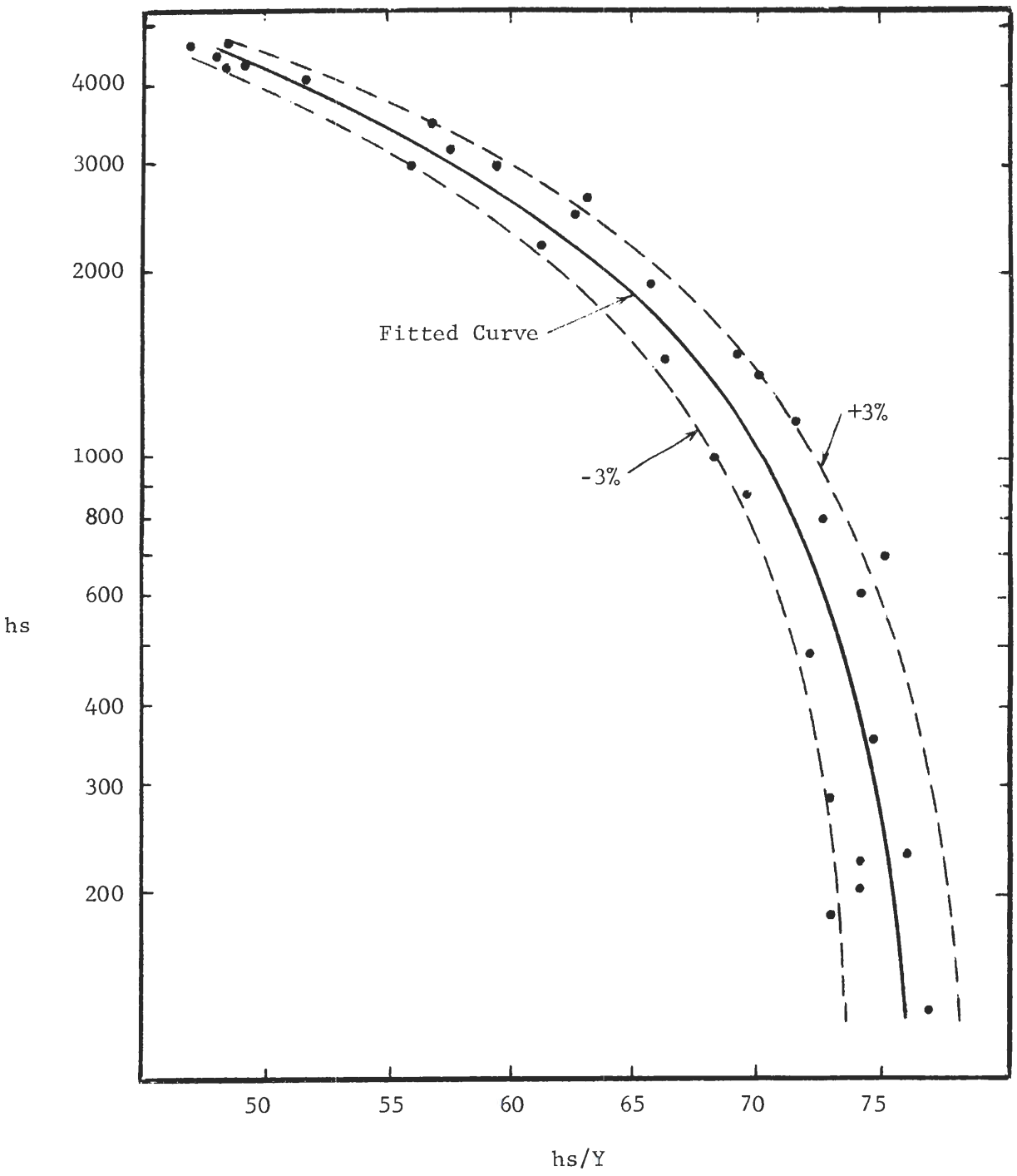

Figure 27. Calibration Curve for Carbon Dioxide Analysis

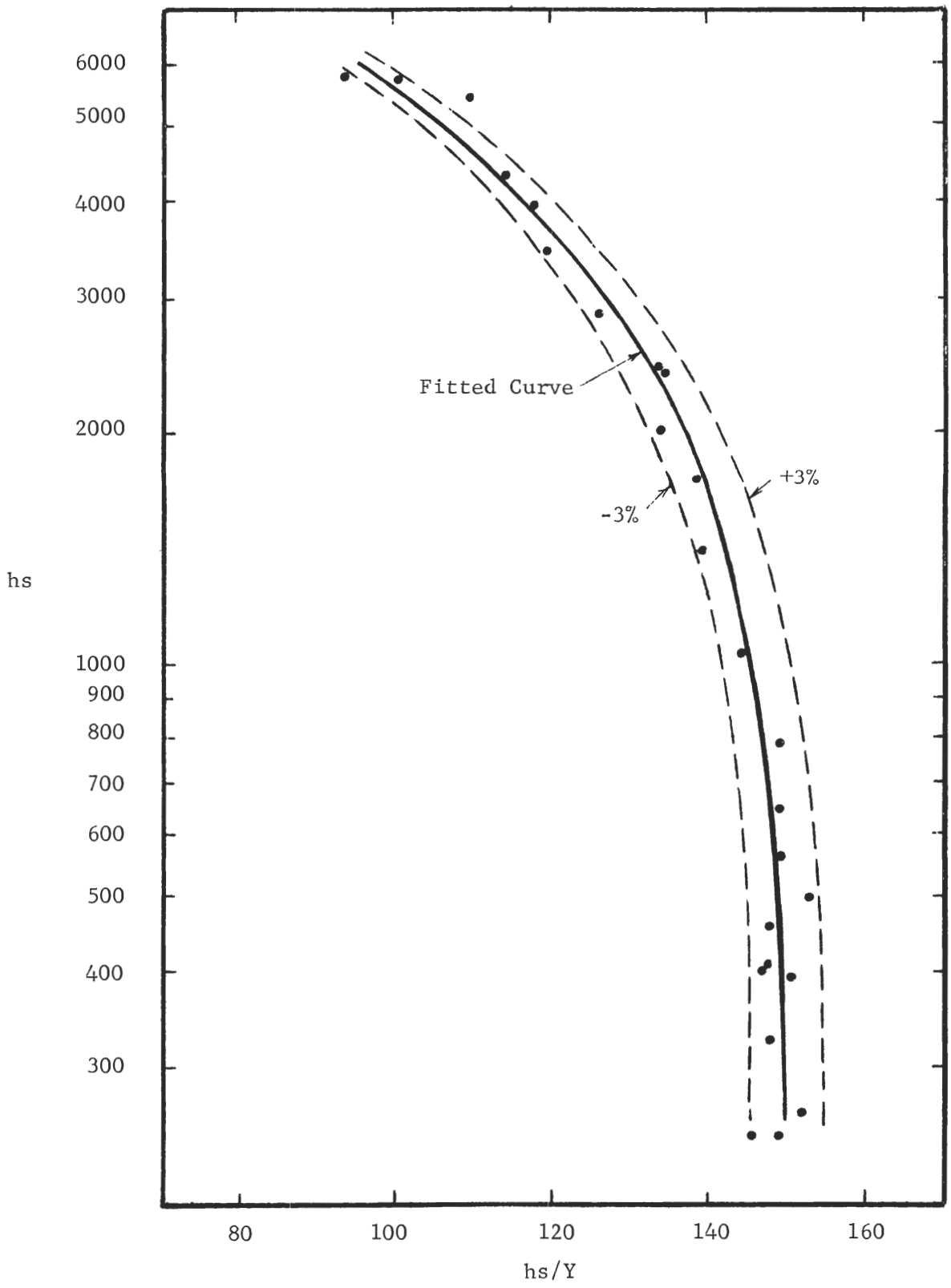

Figure 28. Calibration Curve for Methane Analysis

results of most of the analyses for the individual components totaled 100 per cent to within 2 per cent. These values were adjusted to total 100 per cent exactly by linear proportioning.

No chromatograph calibration with the sample mixing buret was performed upon completion of the adsorption experiments. There is reason to believe such a calibration was unnecessary. The binary and ternary gas mixtures used for the experiments were all analyzed on the chromatograph during the final month of experimentation using the reference standards for daily correction as described above. The mixtures were all found to be unchanged from the original analytical results for each.

APPENDIX D

EXPERIMENTAL PROCEDURES

Pure Isotherm Determination

1. Preliminary steps:

   a) Water thermostat turned on and system at temperature equilibrium.

   b) Ice in thermocouple reference bath.

   c) Evacuate adsorption chamber.

   d) Record barometric pressure.

   e) If reservoir does not contain desired gas from previous run, fully evacuate.

2. Install cryostat and wait for equilibrium at desired temperature.

3. Record thermostat, cryostat and room temperature.

4. Charge gas into supply reservoir. Pressure gauge P3 valve open.

5. When ready to begin:

   a) Record reading on reservoir manometer.

   b) Start the cryostat temperature recorder.

6. Be sure the adsorption space is fully evacuated and then close the evacuation valve.

7. Open the isolating valve which allows gas to flow from the reservoir to the adsorption space.

8. Wait for the pressure to reach a stable value and record the manometer reading and close the isolating valve.

9. Recharge the supply reservoir.

10. Wait for pressure to reach a stable value and then record. Check the cryostat temperature with the calibrated thermocouple and potentiometer system.

11. Repeat steps 7 through 10 until an initial pressure of two atmospheres is no longer adequate in the supply reservoir. Then close the manometer valve and read all pressures from pressure gauge P3 which has been connected to the reservoir system from the start. Repeat steps 7 through 10 until the pressure in the adsorption space reaches the desired limit for the isotherm determination.

This completes the experimental procedure. The results are obtained by FORTRAN program ISTHRM.

For this procedure, inputs to computer program ISTHRM are:

1) Run No.

2) Gas identification

3) Barometric Pressure

4) Cryostat temperature

5) Room temperature

6) Water bath temperature

7) Identifier for pressure device used

8) Pressure readings before and after opening isolating valve. Manometer readings are read in as individual legs and converted to pressure within the program.

Program output:

1) Step No.

2) Absolute pressure

3) Amount adsorbed in millimoles/gm Carbon

4) Compressibilities for various portions of the system as calculated by subroutine BWRMXZ

Fortran program ISTHRM used equation (I-1) to solve each adsorption data point by a material balance. Volumes for the apparatus are within the program. The material balance is performed in moles of the substance. Imperfect gas behavior is accounted for by determining a compressibility factor at each set of pressure-temperature conditions by use of the BWR equation in subroutine BWRMXZ.

Mixture Isotherm Procedure

1. Preliminaries:

a) Water thermostat on and at temperature equilibrium.

b) Ice in thermocouple reference bath.

c) Adsorbent fully regenerated and at 100 milli-Torr or less pressure.

d) Record barometric pressure.

e) Gas supply connected and purge reservoir charged with pure hydrogen.

f) Gas chromatograph running and stabilized.

g) Record reading on positive displacement meter connected to effluent gas.

h) Record room and water thermostat temperatures.

2. Open feed gas supply valve to adsorption space and set pressure regulator to approximate pressure desired.

3. Install cryostat and set controls as necessary to reach desired temperature. Cryostat mixer turned on. When near operating

operating temperature, set temperature controls to operate automatically and start cryostat temperature recorder with reduced range set for 0.5 milli-volt.

4. The vacuum pump is left operating and evacuating the sample reservoir during this period.

5. When the cryostat reaches operating temperature, open the adsorption space outlet valve which allows feed gas to flow. Adjust the outlet rate to 100 to 200 cc/minute.

6. Adjust the feed gas pressure regulator if necessary.

7. Analyze the feed gas on the gas chromatograph.

8. Analyze appropriate reference cylinders on the gas chromatograph.

9. Analyze the effluent gas. Record all analyses, pressure and temperature readings as they are taken on the experiment record sheet.

10. Repeat steps 6 through 9 until the effluent analysis is equal to the feed gas analysis. When the two are equal, close the vacuum valve to the sample reservoir and record the adsorption space pressure.

11. Close the outlet and then the inlet to the adsorption space. These two should be closed as simultaneously as practical to keep the pressure within this part of the system at the same value which was maintained while the gas was flowing. Record the pressure after the adsorption space inlet and outlet valves are closed.

12. Open the valve from the adsorption space to the sample reservoir. For low pressure experiments when the mercury manometer is being used to read the adsorption space pressure, this manometer is closed before allowing flow to the sample reservoir. The sample reservoir is

never allowed to exceed 7 PSIG so several depressurization steps may be required.

13. The sample reservoir mixer is turned on each time the vessel is filled and the pressure readings from the sample manometer are recorded when a constant pressure is reached. Be sure the isolating valve between the adsorption space and the reservoir is closed before recording the pressure and analyzing.

14. The electric heaters are attached to the adsorbent cell after the cryostat is removed. The surface thermocouple is placed in position and the heaters and thermocouple wrapped with blanket type insulation. The heaters are turned on and the temperature recorder is switched to the surface thermocouple.

15. After the sample reservoir pressure is recorded, withdraw a portion of the contents into the sample collector and analyze one to two batches in the chromatograph. Vent the contents of the sample collector and analyze a second portion of the reservoir contents to verify that the batch was well mixed.

16. When the analysis of the gas in the sample reservoir is complete, evacuate the sample reservoir to 100 milli-Torr or less.

17. Open the valve between the adsorption space and the sample reservoir again repeating steps 12, 13, 15 and 16. When the pressure in the sample reservoir stays below one atmosphere and the adsorbent cell has reached 360 K, open the purge valve slowly and allow at least 500 cc or as much hydrogen as is required to raise the sample reservoir pressure to a positive value.

18. When the amount of both methane and carbon dioxide in the

analyzed sample is below 2% and the pressure of the adsorbent space connected to the sample reservoir before opening the purge valve is 2 PSIA or less, the adsorbate may be considered fully removed from the adsorbent.

19. Recheck room and water thermostat temperatures and barometric pressure.

20. Pressure gauge readings are all corrected before input to the computer program by using calibration curves for each gauge. This completes the experimental procedure.

Input to computer program MXADSB includes the following:

1) Run No.

2) Barometric pressure

3) Cryostat temperature

4) Water thermostat temperature

5) Room temperature

6) Feed gas composition

7) Pressure of experiment

8) For each sample:

   a) Composition

   b) Sample reservoir manometer readings

   c) Purge gas reservoir before and after flowing sweep gas

   d) Adsorbent cell temperature

Output from the program:

1) Absolute pressure of experiment

2) Amount of methane and carbon dioxide adsorbed per gram of adsorbent

3) Mixture compressibilities for various parts of the system from subroutine BWRMXZ

Fortran program MXADSB used equation (G-5) in Appendix G to determine the moles of each component adsorbed on the adsorbent sample. Pressure, temperature, gas composition and apparatus dead space volume are known. Imperfect gas behavior in the dead space is calculated by using a compressibility factor determined from a BWR equation solved by Newton-Raphson interation in subroutine BWRMXZ.

APPENDIX E

EXPERIMENTAL DATA

Table 6 gives the experimental data for the three methane isotherms. Table 8 gives comparable data for carbon dioxide. Each isotherm set is identified by the date of the experiment. These results are from Fortran computer program ISTHRM which is briefly described in Appendix D.

All of the experimental values for each data set were used as input to a least-squares fitting program to find a functional form which fitted the data within the estimated experimental accuracy. The equation which gave the best fit for all six methane and carbon dioxide isotherms is

$$\ln N = k_1 + k_2(\ln Ps/P)^2 \qquad \text{(III-4)}$$

Values for k_1, k_2, and Ps are shown in Table 5 based on the use of N in milligram-moles adsorbed per gram of carbon and P in pounds per square inch absolute.

Table 5. Constants for Fitted Isotherm Equations

Isotherm	k_1	k_2	Ps
Methane at 301.4 K	1.8431	-0.0605	1004.1
260.4	1.9519	-0.0528	352.4
212.7	2.0510	-0.0438	57.7
Carbon Dioxide at 301.4	1.9642	-0.7899	668.1
260.2	2.1215	-0.0766	284.3
212.7	2.2610	-0.0805	54.05

The calculated values for Gibbs adsorption from the fitted equations are given in Table 6 for methane and in Table 8 for carbon dioxide. Total adsorption was also calculated and is presented in these two tables. The Gibbs adsorption value and the Dubinin-Nikolaev[31] temperature dependent model described in Chapter IV for adsorbate molar volume were used to calculate total adsorption. Only Gibbs adsorption values were used in subsequent calculations.

Table 10 presents the results of the binary mixture adsorption experiments of this study. Table 11 gives the results for the ternary gas mixtures. Fortran program MXADSB briefly described in Appendix D calculated Gibbs adsorption values. A separate program calculated total adsorption using the same adsorbate volume model as the pure isotherms described above together with equation (IV-13). Total adsorption is presented to show it is not significantly different from Gibbs adsorption for the conditions of this investigation.

Tables 10 and 11 show the calculated adsorbate composition. The amount of hydrogen adsorbed was assumed negligible as it was below the limits of accuracy for the apparatus. Thus the adsorbates shown in Table 11 for ternary gas mixtures are reported as binary solutions.

Adsorption enhancement factors defined as

$$\phi A = \frac{Y_i P}{P^\circ(N_i, T)} \qquad \text{(V-5)}$$

are shown in Tables 10 and 11 for the methane and carbon dioxide. These values were manually calculated. The uncertainty of these values is in the order of 13% due largely to the experimental uncertainty of both the pure and mixture adsorption values which are used for the denominator.

The adsorption enhancement factor is discussed in Chapter V.

The relative volatility α defined by equation (V-2) is shown in Tables 10 and 11. This quantity is discussed in Chapter V.

Tables 12 and 13 give a comparison of adsorbate compositions for the mixtures of this investigation. All binary mixture results are in Table 12 and ternaries are in Table 13. The calculated experimental adsorbate mole fractions for methane and carbon dioxide from Tables 10 and 11 are repeated for convenience. All values shown in these tables were computed in Fortran programs. One of the calculation methods compared in this table is the empirical relation of Lewis et al.[28] which is

$$\sum_{1}^{i} \frac{Ni}{N_i^\circ} = 1 \qquad \text{(E-1)}$$

which directly implies equation (IV-20). Lewis et al.[28] indicated that N_i° in equation (E-1) should be at P and T for the mixture isotherm. However, it is conceivable that there will be conditions where N_i° at the component partial pressure $Y_i P$ and T might give a more accurate prediction. Tables 12 and 13 allow this comparison for all of the mixture data from this investigation. The calculated adsorbate molar fractions from the experimental results are identified as X_M for methane and X_D for carbon dioxide. The result of the calculated mole fraction using equation (IV-20) at N_i° (P,T) is identified by the additional subscript "T ". The sum of X_{MT} plus X_{DT} is shown under the second to last column under the headings "Sum " and "T". The result of the calculations using equation (IV-20) with N_i° ($Y_i P$,T) has the added subscript "P". The sum

of X_{MP} plus X_{DP} is in the last column under "P". All N_i° values in these calculations were obtained from the fitted pure isotherm equations.

The tables also show the result of calculating the adsorbate mole fraction using the equi-potential concept as expressed in equation (IV-10) with the use of equation (IV-11). This is identified with the added subscript "G".

It can be seen by comparing the experimental adsorbate mole fractions with the results calculated from the Lewis et al.[28] empirical relation and the equi-potential concept that the latter gives consistently more accurate results for both the binary and ternary gas mixtures. Between the two approaches to the Lewis empirical method, system total pressure for the determination of the pure isotherm value does not give a consistently more accurate result than component partial pressure. The sums are reported as an added convenience to show the agreement with equation (E-1).

Figure 29 shows an Adsorption Potential Theory characteristic curve for adsorbate volume $N\bar{V}_i$ plotted against adsorption potential $\frac{T}{\bar{V}_i} \ln (\frac{fs}{f})_i$. This plot was constructed from the six pure isotherms for methane and carbon dioxide determined in this investigation. This plot uses adsorbate molar volume $\bar{V}i$ in both the ordinate and the abscissa as a pressure dependent variable. The molar volume is taken as the saturated liquid corresponding to a pressure equal to Pg where

$$Pg = (\frac{Y}{X})_i P \qquad \text{(IV-12)}$$

Sources for the physical properties are given in Chapter V. Fugacities were calculated using the BWR equation and an explicit

fugacity relation and constants given by Orye.[32] Saturated fugacity values used depend on temperature and are reported in Table 2 located in Chapter V. The fitted pure isotherm equations were used with pressure increments as the independent variable to calculate the ordinate for Figure 29.

Figure 30 shows a plot of characteristic curve values with the binary mixture experimental data of this investigation. For this plot all molar volumes are at the component normal boiling point. The molar volume in the ordinate is obtained from equation (IV-13) while the abscissa uses the pure component value. Fugacities were determined as described for Figure 29 above. The eye-fitted characteristic curve presented as Figure 10 constructed from pure component isotherms using the same molar volume method is shown as a heavy solid line.

Figure 31 shows the results from plotting the same data as Figure 30 with the exception that the adsorbate molar volumes used in ordinate and abscissa are pressure dependent as described for Figure 29 above. Except for adsorbate molar volume, all values were determined as described for Figure 30 above. The characteristic curve of Figure 29 is shown as a heavy solid line on Figure 31.

Figure 32 shows points calculated from the ternary gas mixture data of this investigation. Construction of this plot was the same in every detail as the method used for Figure 30. The characteristic curve of Figure 10 is shown as a heavy solid line.

Figure 33 is the same as Figure 32 with the exception that it follows the variable adsorbate molar volume method used for Figure 31. The characteristic curve of Figure 29 is shown as a heavy solid line on this plot.

Table 6. Pure Methane Experimental Values

301.4 K	PSIA	N	PSIA	N
	8.8	0.567	8.9	0.552
	17.0	0.909	20.6	1.005
	25.6	1.193	57.3	1.882
	40.4	1.510	99.2	2.507
	64.9	2.020	(Mar. 20, 1972)	
	100.3	2.535	6.8	0.489
	(Mar. 21, 1972)		19.4	1.009
	10.4	0.616	26.5	1.233
	20.9	1.012	41.9	1.620
	27.6	1.216	59.4	1.983
	46.3	1.678	79.3	2.298
	71.6	2.134	100.1	2.572
	87.7	2.380	(Mar. 21, 1972)	
	112.0	2.686		
	(Mar. 20, 1972)			

260.2 K	PSIA	N	PSIA	N
	5.4	0.885	5.4	0.884
	14.7	1.620	14.8	1.621
	30.1	2.345	30.3	2.362
	57.0	3.125	56.3	3.162
	94.6	3.800	95.3	3.837
	(Mar. 30, 1972)		(May 3, 1972)	

Table 6. (Continued)

212.7 K	PSIA	N	PSIA	N
	0.8	0.721	0.7	0.720
	4.0	1.939	4.0	1.938
	32.1	4.461	32.0	4.423
	78.3	5.612	78.0	5.555
	105.4	5.979	106.0	5.923
	(Mar. 29, 1972)		(Mar. 29, 1972)	

N is given in milligram-moles/gram of carbon

Table 7. Pure Methane Isotherm Fitted Values For Gibbs and Total Adsorption

		N in milligram-mole/ gram carbon	
	Pressure (PSIA)	Gibbs	Total
301.4 K	5.0	0.36	0.36
	15.0	0.83	0.83
	25.0	1.17	1.17
	35.0	1.44	1.45
	45.0	1.67	1.68
	55.0	1.86	1.87
	65.0	2.04	2.06
	75.0	2.19	2.21
	85.0	2.33	2.35
	95.0	2.46	2.49
260.2 K	5.0	0.82	0.82
	15.0	1.61	1.61
	25.0	2.12	2.13
	35.0	2.49	2.50
	45.0	2.79	2.81
	55.0	3.05	3.07
	65.0	3.26	3.29
	75.0	3.45	3.49
	85.0	3.62	3.66
	95.0	3.77	3.82

Table 7. (Continued)

		N in milligram-mole/ gram carbon	
	Pressure (PSIA)	Gibbs	Total
212.7 K	5.0	2.11	2.11
	15.0	3.38	3.39
	25.0	4.06	4.08
	35.0	4.52	4.55
	45.0	4.88	4.92
	55.0	5.15	5.20
	65.0	5.38	5.44
	75.0	5.58	5.65
	85.0	5.75	5.83
	95.0	5.89	5.99

Table 8. Pure Carbon Dioxide Isotherm Experimental Values

301.4	PSIA	N	PSIA	N	PSIA	N
	6.7	1.045	6.8	1.034	4.0	0.748
	14.5	1.737	14.9	1.751	12.0	1.567
	21.3	2.192	21.1	2.161	19.6	2.125
	41.5	3.187	38.9	3.072	44.1	3.323
	63.4	3.928	84.9	4.433	69.8	4.141
	85.8	4.547	120.1	5.191	95.5	4.790
	111.2	5.086	(Mar. 16, 1972)		125.9	5.405
	(Mar. 17, 1972)		6.2	0.898	(May 16, 1972)	
			14.6	1.615		
			21.4	2.064		
			37.8	2.861		
			59.5	3.635		
			92.7	4.490		
			(Mar. 15, 1972)			

260.2 K	PSIA	N	PSIA	N
	2.1	1.172	2.5	1.292
	6.2	2.344	6.8	2.418
	11.5	3.305	23.6	4.526
	33.2	5.323	48.4	6.282
	61.7	6.704	91.4	7.486
	104.1	7.744	(April 3, 1972)	
	(Mar. 31, 1972)			

Table 8. (Continued)

212.7 K	PSIA	N	PSIA	N	PSIA	N
	0.5	1.391	0.5	1.405	0.4	1.545
	1.0	2.775	1.1	2.782	1.2	2.844
	9.3	7.286	2.4	4.121	2.3	4.180
	38.7	9.787	6.7	6.396	4.3	5.464
	(Apr. 18, 1972)		18.8	8.714	32.1	9.391
			24.1	9.101	(Apr. 5, 1972)	
			28.4	9.321		
			(Apr. 4, 1972)			

N is given in milligram-moles/gram carbon

Table 9. Pure Carbon Dioxide Isotherm Fitted Values for Gibbs and Total Adsorption

	Pressure PSIA	N in milligram-mole/ gram carbon	
		Gibbs	Total
301.4 K	5.0	0.78	0.78
	15.0	1.77	1.77
	25.0	2.43	2.44
	35.0	2.93	2.94
	45.0	3.33	3.35
	55.0	3.66	3.68
	65.0	3.95	3.98
	75.0	4.19	4.23
	85.0	4.41	4.46
	95.0	4.60	4.65
260.2 K	5.0	2.08	2.08
	15.0	3.89	3.90
	25.0	4.88	4.90
	35.0	5.55	5.57
	45.0	6.03	6.06
	55.0	6.41	6.46
	65.0	6.70	6.76
	75.0	6.95	7.02
	85.0	7.15	7.23
	95.0	7.31	7.40

Table 9. (Continued)

	Pressure PSIA	N in milligram-mole/ gram carbon	
		Gibbs	Total
212.7 K	5.0	5.93	5.93
	10.0	7.50	7.51
	15.0	8.29	8.31
	20.0	8.77	8.79
	25.0	9.07	9.10
	30.0	9.27	9.31
	35.0	9.41	9.46
	40.0	9.50	9.56

Table 10. Binary Mixture Experimental Results with Calculated Variables

Mixture	Temp. K	Pressure PSIA	Adsorption in m-moles/gm carbon Gibbs		Total		Mole Fraction (1)		Enhancement Factor		α (2)
			N_M	N_D	N_M	N_D	X_M	X_D	ϕ_{AM}	ϕ_{AD}	
	301.4	18.8	0.11	1.44	0.11	1.45	.071	.929	3.21	1.40	3.01
	301.4	44.4	0.24	2.52	0.24	2.53	.086	.914	2.78	1.38	2.47
Y_M=0.188	301.4	75.3	0.36	3.23	0.37	3.25	.100	.900	3.08	1.42	2.08
	301.4	78.8	0.30	3.34	0.31	3.37	.083	.917	3.70	1.39	2.54
Y_D=0.812	260.2	19.1	0.16	3.93	0.16	3.94	.039	.961	4.49	1.03	5.75
	260.2	43.1	0.24	5.00	0.25	5.02	.047	.953	6.23	1.30	4.74
	260.2	75.9	0.28	6.23	0.30	6.28	.044	.956	7.93	1.23	5.08
	301.4	18.9	0.32	1.17	0.33	1.17	.216	.784	2.19	1.19	3.59
	301.4	19.0	0.32	1.22	0.32	1.22	.208	.792	2.20	1.14	3.78
	301.4	42.3	0.53	1.72	0.54	1.73	.235	.765	2.63	1.52	3.22
	301.4	66.8	0.68	2.45	0.69	2.46	.216	.784	2.82	1.34	3.59
	301.4	69.4	0.71	2.33	0.73	2.34	.235	.765	2.88	1.53	3.24
Y_M=0.498	260.2	17.6	0.48	2.74	0.48	2.75	.148	.852	3.02	1.13	5.73
Y_D=0.502	260.2	42.3	0.67	3.82	0.68	3.83	.149	.851	5.02	1.50	5.69
	260.2	42.7	0.72	3.89	0.73	3.90	.155	.845	4.62	1.44	5.40
	260.2	67.0	0.77	4.93	0.80	4.95	.136	.864	6.42	1.67	6.32
	212.7	20.2	0.30	7.54	0.31	7.55	.038	.962	-	0.98	25.1
	212.7	40.0	0.30	8.51	0.33	8.54	.034	.966	-	1.13	28.0

Table 10. (Continued)

Mixture	Temp. K	Pressure PSIA	Adsorption in m-moles/gm carbon Gibbs N_M	Gibbs N_D	Total N_M	Total N_D	Mole Fraction (1) X_M	Mole Fraction (1) X_D	Enhancement Factor ϕ_{AM}	Enhancement Factor ϕ_{AD}	α (2)
	301.4	18.6	0.59	0.52	0.59	0.52	.531	.469	1.52	1.36	3.43
	301.4	44.9	0.95	0.93	0.96	0.94	.505	.495	1.98	1.53	3.80
	301.4	77.3	1.25	1.22	1.26	1.22	.505	.495	2.20	1.91	3.80
Y_M=0.795	301.4	89.1	1.32	1.32	1.34	1.32	.501	.499	2.33	1.84	3.87
	260.2	19.3	1.08	1.37	1.08	1.37	.439	.561	1.92	1.72	4.95
Y_D=0.205	260.2	40.0	1.52	1.91	1.53	1.91	.443	.557	2.30	2.00	4.88
	260.2	74.3	1.82	2.70	1.86	2.71	.403	.597	3.19	2.11	5.75

Notes: (1) Mole fractions based on Gibbs adsorption

(2) $\alpha = X_D Y_M / X_M Y_D$

Table 11. Ternary Mixture Experimental Results with Calculated Variables

Mixture	Temp. K	Pressure PSIA	Adsorption in m-moles/gm carbon Gibbs N_M	Gibbs N_D	Total N_M	Total N_D	Mole Fraction (1) X_M	Mole Fraction (1) X_D	Adsorption Enhancement ϕ_{AM}	Adsorption Enhancement ϕ_{AD}	α (2)
	301.4	17.7	0.02	0.32	0.02	0.32	.061	.939	-	1.33	3.24
	301.4(3)	86.9	0.07	1.08	0.07	1.08	.058	.942	2.25	1.19	3.45
	301.4(4)	87.3	0.07	1.09	0.07	1.09	.060	.940	2.26	1.20	3.35
	301.4	224.5	0.10	1.82	0.10	1.83	.053	.947	4.64	1.45	3.82
	301.4	234.8	0.11	1.78	0.11	1.79	.059	.941	4.43	1.54	3.40
Y_M=0.0207	301.4	512.0	0.14	2.64	0.15	2.65	.052	.948	7.06	1.75	3.88
Y_D=0.0977	260.2	17.1	0.04	1.25	0.04	1.25	.029	.971	-	0.76	7.14
Y_H=0.882	260.2	84.3	0.12	2.68	0.12	2.68	.041	.959	4.36	1.13	4.90
	260.2	85.9	0.12	3.17	0.12	3.18	.036	.964	4.44	0.85	5.65
	260.2	216.3	0.14	4.30	0.14	4.31	.032	.968	8.95	1.14	6.42
	260.2	497.0	0.21	5.27	0.22	5.31	.039	.961	10.3	1.59	5.20
Y_M=0.0660	301.4	25.4	0.10	0.36	0.10	0.36	.212	.788	1.67	1.00	3.52
Y_D=0.0695	301.4(5)	90.9	0.22	0.93	0.22	0.93	.192	.808	2.60	1.05	4.00
Y_H=0.864	301.4(6)	94.9	0.24	0.93	0.25	0.93	.208	.792	2.60	1.10	3.62
	301.4	210.3	0.34	1.44	0.35	1.44	.194	.806	3.15	1.37	3.95
	301.4	501.8	0.49	2.13	0.50	2.14	.187	.813	4.66	1.75	4.14

Notes: (1) Mole fraction based on Gibbs adsorption

(2) α equals $X_D Y_M / X_M Y_D$

(3) Experiment run on May 19, 1972

(4) Experiment run on July 25, 1972

(5) Experiment run on July 5, 1972

(6) Experiment run on June 1, 1972

Table 11. (Continued)

Mixture	Temp. K	Pressure PSIA	Adsorption in m-moles/gm carbon Gibbs N_M	Gibbs N_D	Total N_M	Total N_D	Mole Fraction (1) X_M	X_D	Adsorption Enhancement ϕ_{AM}	ϕ_{AD}	α (2)
	301.4	508.0	0.49	2.17	0.50	2.18	.184	.816	4.72	1.75	4.20
	260.2	22.9	0.21	1.17	0.21	1.17	.151	.849	1.50	0.80	5.36
	260.2	92.2	0.41	2.19	0.41	2.19	.157	.843	2.77	1.16	5.10
Y_M=0.0660	260.2	205.8	0.51	3.12	0.52	3.12	.141	.859	4.38	1.49	5.78
Y_D=0.0695	260.2	208.0	0.52	3.16	0.52	3.17	.140	.860	4.29	1.49	5.82
Y_H=0.864	260.2	486.0	0.51	4.13	0.53	4.15	.110	.890	10.3	1.99	7.72
	260.2	507.0	0.56	4.30	0.58	4.32	.115	.885	9.56	1.89	7.28
	212.7	19.7	0.32	3.70	0.32	3.70	.079	.921	-	0.68	11.0
	212.7	33.4	0.35	4.23	0.35	4.23	.077	.923	-	0.86	11.4
	212.7	89.2	0.40	5.64	0.41	5.65	.067	.933	-	1.35	13.3
Y_M=0.108	260.2	21.2	0.38	0.48	0.38	0.48	.437	.563	1.09	1.20	4.86
Y_D=0.0286	260.2	37.1	0.54	0.72	0.54	0.72	.430	.570	1.21	0.96	5.01
Y_H=0.863	260.2	475.0	1.52	3.43	1.55	3.44	.307	.693	3.31	1.19	8.54

Notes: See previous page for notes (1) to (6)

Table 12. Binary Mixtures - Adsorbate Mole Fraction Relations

Mixture	Temp K	Pressure PSIA	Methane X_M	X_{MT}	X_{MP}	X_{MG}	Carbon Dioxide X_D	X_{DT}	X_{DP}	X_{DG}	Sum T	Sum P
	301.4	18.8	.071	.115	.418	.07	.929	.706	.807	.93	.820	1.22
		44.4	.086	.143	.438	.06	.914	.761	.846	.94	.904	1.28
		75.3	.100	.164	.452	.06	.900	.768	.839	.94	.932	1.29
Y_M=.188		78.8	.083	.135	.370	.06	.917	.781	.851	.94	.916	1.22
Y_D=.812	260.2	19.1	.039	.086	.242	.05	.961	.902	.994	.95	.988	1.24
		43.1	.047	.089	.218	.05	.953	.841	.902	.95	.930	1.12
		75.9	.044	.082	.181	.05	.956	.895	.943	.95	.976	1.12
	301.4	18.9	.216	.333	.548	.25	.784	.572	.914	.75	.905	1.46
		19.0	.208	.327	.538	.25	.792	.591	.945	.75	.918	1.48
		42.3	.235	.330	.508	.23	.765	.534	.782	.77	.864	1.29
		66.8	.216	.327	.484	.22	.784	.613	.855	.78	.914	1.34
Y_M=0.498		69.4	.235	.339	.500	.22	.765	.574	.796	.78	.912	1.30
Y_C=0.502	260.2	17.6	.148	.270	.403	.20	.852	.654	.931	.80	.924	1.33
		42.3	.149	.245	.344	.18	.851	.645	.837	.82	.890	1.18
		42.7	.155	.262	.367	.18	.845	.656	.850	.82	.918	1.22
		67.0	.136	.234	.317	.18	.864	.729	.901	.82	.963	1.22
	212.7	20.2	.038	.079	.104	.086	.962	.859	1.002	.914	.938	1.11
		40.0	.034	.064	.080	.081	.966	.896	.970	.919	.960	1.05

Table 12. (Continued)

Mixture	Temp K	Pressure PSIA	Methane X_M	X_{MT}	X_{MP}	X_{MG}	Carbon Dioxide X_D	X_{DT}	X_{DP}	X_{DG}	Sum T	Sum P
	301.4	18.6	.531	.615	.721	.57	.469	.257	.851	.43	.873	1.57
		44.9	.505	.573	.655	.54	.495	.280	.743	.46	.853	1.40
		77.3	.505	.559	.630	.53	.495	.287	.666	.47	.847	1.30
Y_M=.795		89.1	.501	.553	.620	.53	.499	.293	.656	.47	.846	1.28
Y_C=.205												
	260.2	19.3	.439	.581	.658	.50	.561	.314	.771	.50	.895	1.43
		40.0	.443	.572	.636	.48	.557	.328	.675	.52	.900	1.31
		74.3	.403	.529	.580	.47	.597	.389	.689	.53	.918	1.27

Note: 1. Total Sum = $\sum \frac{Ni(Y_i P, T)}{\overset{\circ}{Ni}(P, T)}$

2. Partial Sum = $\sum \frac{Ni(Y_i P, T)}{\overset{\circ}{Ni}(P_i, T)}$

Table 13. Ternary Mixtures - Adsorbate Mole Fraction Relations

Mixture	Temp K	Pressure PSIA	Methane X_M	X_{MT}	X_{MP}	X_{MG}	Carbon Dioxide X_D	X_{DT}	X_{DP}	X_{DG}	Sum T	Sum P
	301.4	17.7	.061	.023	.785	.08	.939	.163	1.100	.92	.186	1.88
		86.9	.058	.028	.462	.07	.942	.242	.911	.93	.270	1.37
		87.3	.060	.029	.480	.07	.940	.245	.919	.93	.274	1.40
Y_M=0.0207		224.5	.053	-	.301	.06	.947	-	.810	.94	-	1.11
		234.8	.059	-	.318	.06	.941	-	.771	.94	-	1.09
Y_C=0.0977		512.0	.052	-	.223	.06	.948	-	.752	.94	-	.975
Y_M=0.8816												
	260.2	17.1	.029	.021	.389	.06	.971	.301	1.340	.94	.323	1.73
		84.3	.041	.032	.305	.05	.959	.376	.947	.95	.408	1.251
		85.9	.036	.033	.308	.05	.964	.443	1.108	.95	.476	1.42
		216.3	.032	-	.187	.05	.968	-	.945	.95	-	1.13
		497.0	.039	-	.166	.04	.961	-	.854	.96	-	1.02
	301.4	25.4	.212	.082	.726	.28	.788	.147	1.208	.72	.229	1.93
		90.9	.192	.092	.533	.25	.808	.206	.991	.75	.298	1.52
		94.9	.208	.100	.570	.25	.792	.203	.960	.75	.303	1.53
Y_M=0.0660		210.3	.194	-	.439	.23	.806	-	.826	.77	-	1.26
Y_C=0.0695		501.8	.187	-	.351	.21	.813	-	.727	.79	-	1.08
Y_M=0.8645		508.0	.184	-	.349	.21	.816	-	.736	.79	-	1.08
	260.2	22.9	.151	.102	.609	.23	.849	.248	1.307	.77	.350	1.92
		92.2	.157	.109	.436	.20	.843	.301	.896	.80	.410	1.33
		205.8	.141	-	.336	.18	.859	-	.820	.82	-	1.16
		208.0	.140	-	.336	.18	.860	-	.827	.82	-	1.16
		486.0	.110	-	.212	.17	.890	-	.754	.83	-	.97
		507.0	.115	-	.230	.17	.885	-	.774	.83	-	1.00

Table 13. (Continued)

Mixture	Temp K	Pressure PSIA	Methane X_M	X_{MT}	X_{MP}	X_{MG}	Carbon Dioxide X_D	X_{DT}	X_{DP}	X_{DG}	Sum T	Sum P
Y_M=0.0660	212.7	19.7	.079	.085	.312	.10	.921	.423	1.19	.90	.508	1.50
		33.4	.077	.079	.255	.10	.923	.451	1.01	.90	.530	1.26
Y_C=0.0695		89.2	.067	.070	.178	.09	.933	.597	.878	.91	.667	1.06
Y_M=0.8645												
Y_M=0.108												
	260.2	21.2	.437	.193	.801	.55	.563	.106	1.29	.45	.300	2.09
Y_C=0.029		37.1	.430	.212	.770	.54	.570	.127	1.141	.46	.339	1.91
Y_N=0.863		475.0	.370	-	.513	.47	.693	-	.926	.53	-	1.44

Note: 1. Total Sum = $\sum \frac{Ni(Y_i P,T)}{\mathring{N}i(P, T)}$

2. Partial Sum = $\sum \frac{Ni(Y_i P,T)}{\mathring{N}i(P_i, T)}$

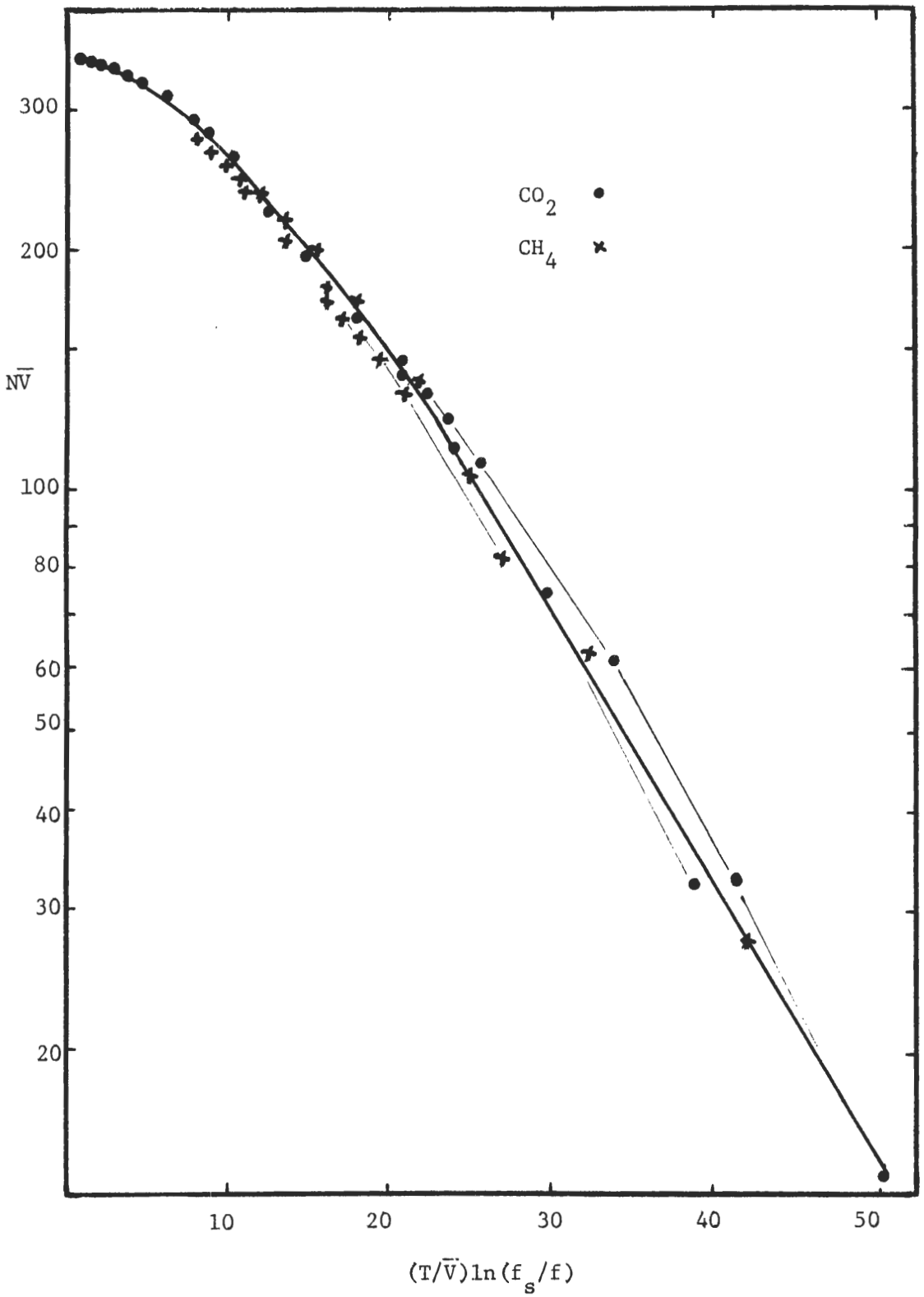

Figure 29. Grant-Manes Characteristic Curve with Variable Molar Volume.

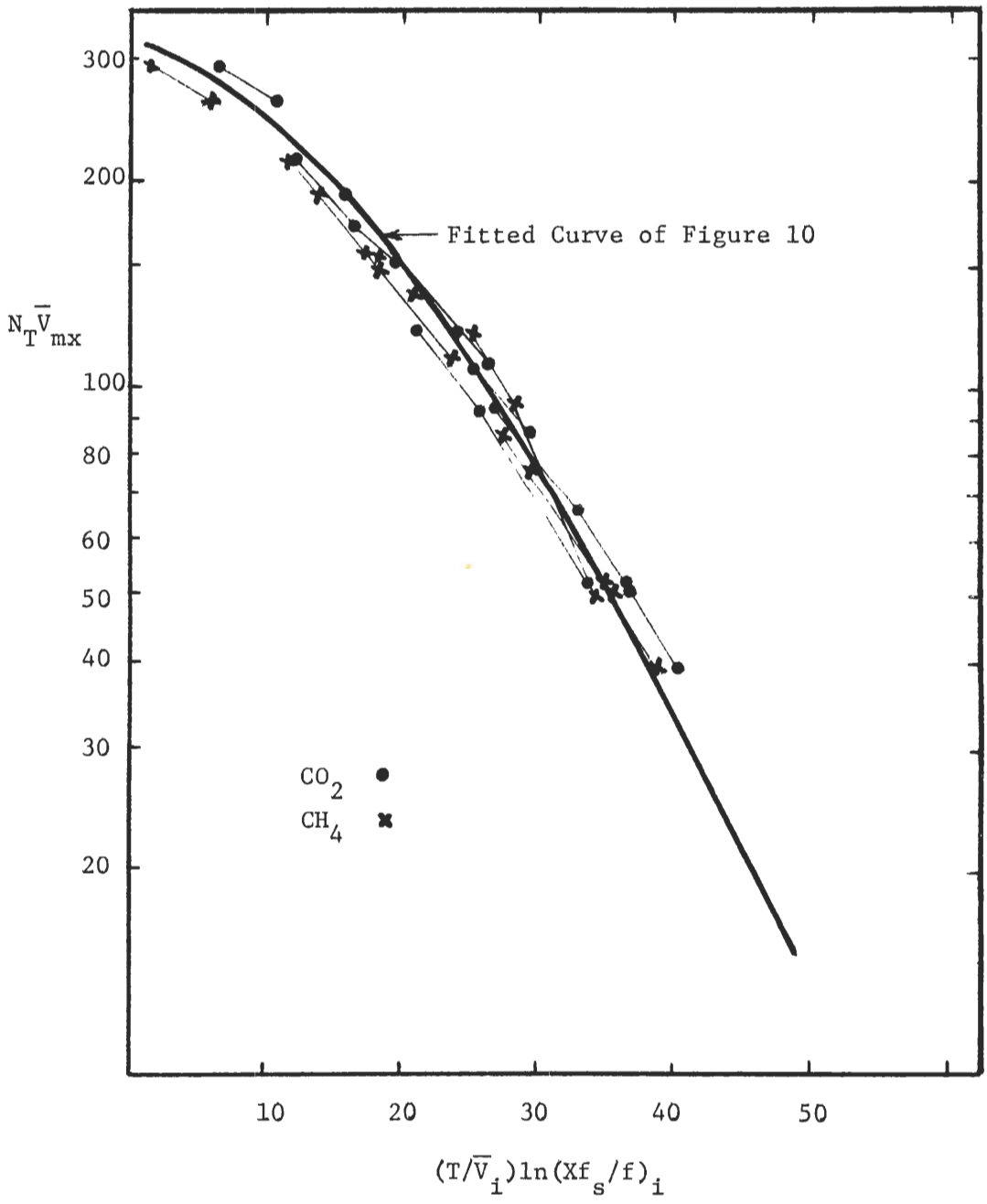

Figure 30. Binary Mixture Characteristic Curve with Constant Molar Volume.

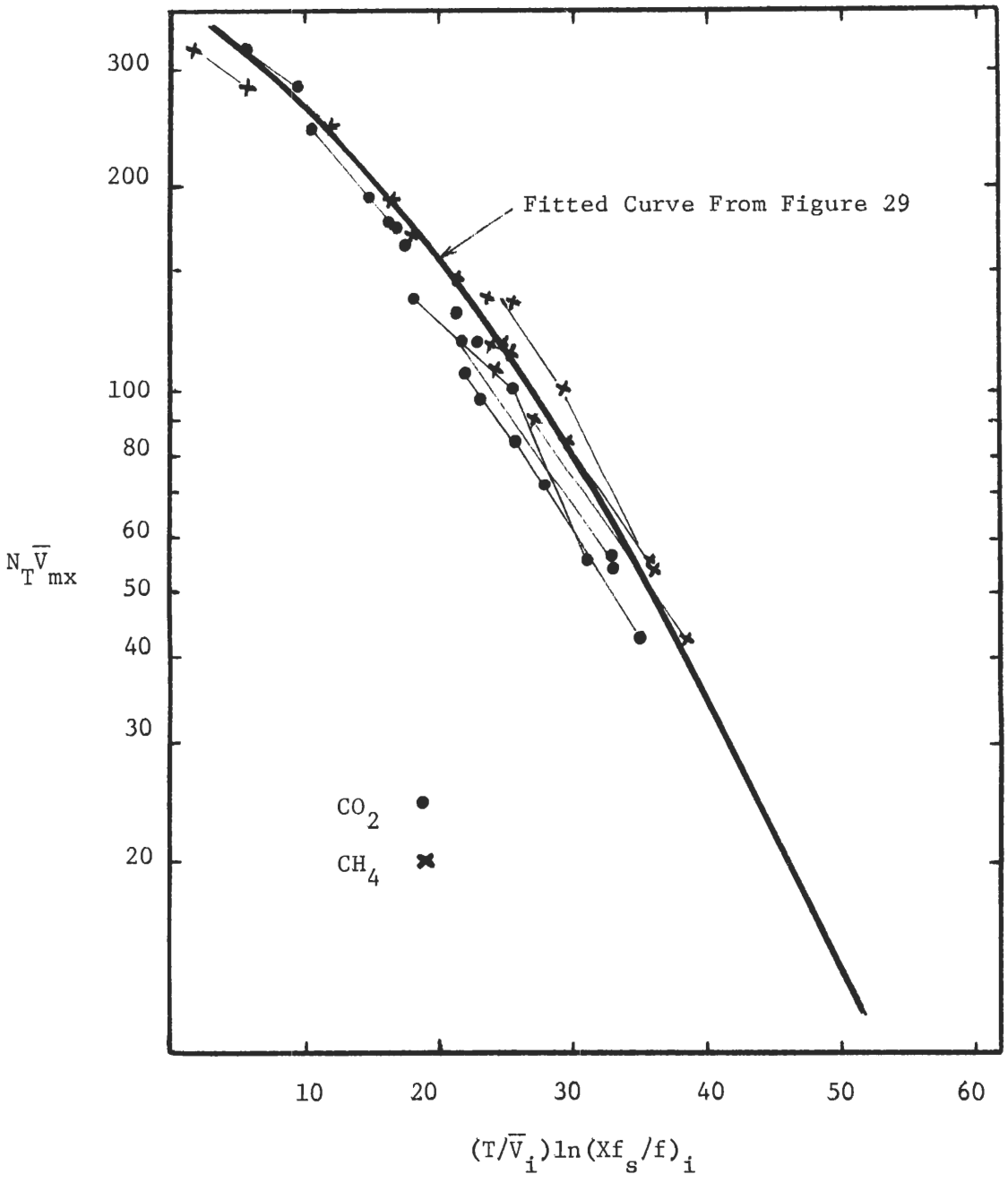

Figure 31. Binary Mixture Characteristic Curve with Variable Molar Volume.

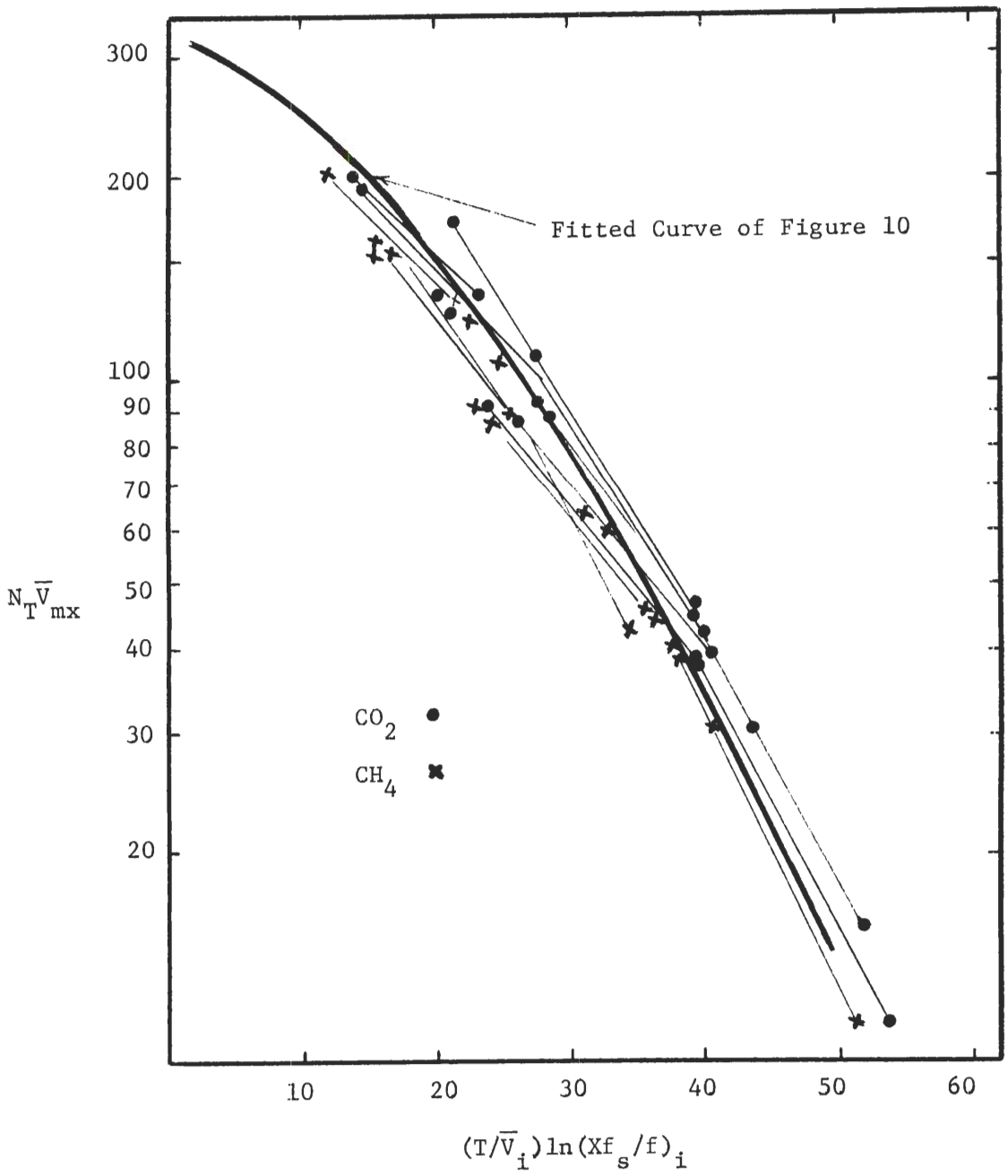

Figure 32. Ternary Mixture Characteristic Curve with Constant Molar Volume.

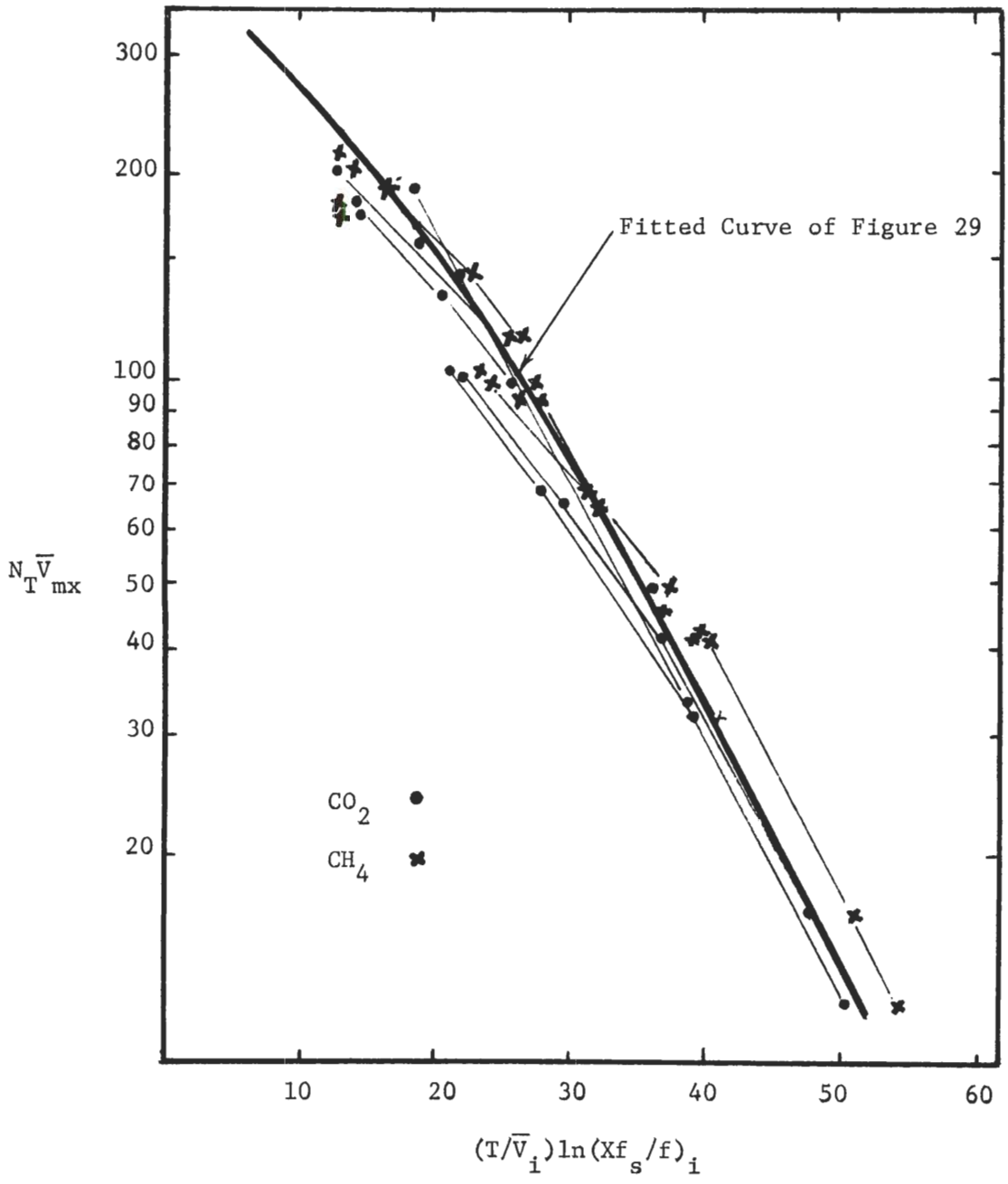

Figure 33. Ternary Mixture Characteristic Curve With Variable Molar Volume.

APPENDIX F

PURITY OF COMPONENT GASES AND MIXTURE PREPARATION

The hydrogen used was supplied by AIRCO and the purity was certified to be 99.97 mole percent. Because this hydrogen was made by the electrolysis of water, no CO_2 or CH_4 contamination would be expected.

The CO_2 used was from Liquid Carbonic and the nominal purity is 99.95 mole percent. Upon receipt of the full cylinder which contained a large fraction of liquid at room temperature, the cylinder was purged at a high rate to eliminate non-condensibles which may have concentrated in the vapor phase.

The methane used was purchased from the Matheson Company and was their Ultra-Pure Grade which is certified to be at least 99.9% pure.

All pure gases were run on the gas chromatograph at maximum sensitivity to verify that the impurities detectable with a peak time less than 10 minutes did not exceed 0.10%. All gases were used without further purification.

All gas mixtures used in this investigation were prepared in this laboratory in evacuated commercial steel gas cylinders. Control of the compositions was accomplished by use of the calibrated pressure gauges on the adsorption apparatus. The cylinders used for mixtures had metal rods or tubes inside and after filling, the cylinders were rotated intermittently for one to two hours and allowed to set overnight before any gas was withdrawn. Analyses performed on the various mixture cylinders in the course of the experiments confirmed that thorough mixing was achieved.

APPENDIX G

ERROR ANALYSIS

All measurements taken in the experiments for this study were for the purpose of determining the number of moles of gas present in parts of the equipment. For a pure gas, the moles present in a known volume may be shown by equation (G-1).

$$N = k(PV/ZT) \tag{G-1}$$

The worst anticipated error in the measurement of N where individual variations are shown by "Δ" notation is given in equation (G-2).

$$\Delta N = \left(\frac{\partial N}{\partial V}\right)_{P,T,Z} \Delta V + \left(\frac{\partial N}{\partial P}\right)_{V,T,Z} \Delta P + \left(\frac{\partial N}{\partial T}\right)_{P,V,Z} \Delta T + \left(\frac{\partial N}{\partial Z}\right)_{P,T,V} \Delta Z \tag{G-2}$$

Evaluating the partial derivatives by using equation (G-1) and dividing by N and multiplying by 100 to obtain per cent relative variation gives equation (G-3).

$$100\left(\frac{\Delta N}{N}\right) = \frac{1}{N}\left[\left(\frac{\partial N}{\partial V}\right)_{P,T,Z} \Delta V + \left(\frac{\partial N}{\partial P}\right)_{V,T,Z} \Delta P + \left(\frac{\partial N}{\partial T}\right)_{P,V,Z} \Delta T + \left(\frac{\partial N}{\partial Z}\right)_{P,V,T} \Delta Z\right](100) = \tag{G-3}$$

$$\left[\frac{\Delta V}{V} + \frac{\Delta P}{P} - \frac{\Delta Z}{Z} - \frac{\Delta T}{T}\right](100)$$

The individual terms in equation (G-3) are seen to be the relative accuracies achieved with each of the measurements. An analysis of readability, calibration certainty and the many factors which go into

the assignment of accuracies to each of the measurements lead to the following values:

$$\Delta V/V = 0.010$$

$$\Delta P/P = 0.0025$$

$$\Delta T/T = 0.00094$$

$$\Delta Z/Z = 0.005$$

Thus, for a pure component, equation (G-3) indicates that the moles can be measured to less than ± 1.84%. Where analysis is required to account for more than one component in a mixture and the accuracy of the analysis is ± 3%, the accuracy for a particular component is ± 4.8%. These accuracies apply to the determination of the moles contained in one part of the system. The adsorption computation is made up of a difference of two calculated quantities as shown in equation (G-4).

(Moles adsorbed) = (Mole admitted) - (Moles in Dead Space) (G-4)

The moles admitted is the result of two calculations, the amount in the reservoir before and after allowing gas into the dead space. Thus the calculation of the number of moles adsorbed depends upon the calculation of three quantities. The uncertainty of the calculated amount adsorbed is not three times the uncertainty of each measurement as the relative values of the individual terms must be taken into account. Since each error may be positive or negative, the probable total error is always less than the maximum error. A more detailed consideration of the actual expected error for any given measurement shows that it is necessary to allow for the actual type of pressure device used,

the level of the readings, and the magnitude of all quantities if a percent error is to be determined.

A different approach to the assignment of a certainty to the entire set of data is to analyze the deviations from a fitted function. The methane isotherms gave fits which had a maximum point deviation of 3.7% for the worst point. The carbon dioxide points were poorer, particularly at low pressures. However, there were significantly more low pressure points measured for carbon dioxide than for methane. At low pressure, a small increment can result in a large percent deviation. For this reason, the very low pressure deviations were discounted when a judgment was made to assign a precision of 5% or better to the carbon dioxide isotherms.

For the mixtures, the certainty of the analysis has been estimated as ± 3%. However, the experimental value for the amount adsorbed is calculated for each component after a summation of the amount of the component in each of the samples as shown in equation (G-5).

$$\text{(Moles of i adsorbed)} = \sum_{i}^{\text{All samples}} \text{(Moles i desorbed)} - \text{(Moles of i in Dead Space)} \quad \text{(G-5)}$$

The accuracy of a particular calculated point will again be seen to depend upon the magnitude of the values which comprise the sum. A general statement of the probable error for the amount adsorbed with the method used in these experiments is shown by equation (G-6).

$$\text{Probable Error of N} = \frac{\sqrt{\sum_{i=0}^{\gamma} (N_i^2 Y_i^2)(\gamma_A^2 + \gamma_A^2)}}{\sum^{\gamma} (N_i Y_i) - N_O Y_O} \qquad \text{(G-6)}$$

where γ = analytical accuracy expressed as a decimal.

Subscripts:

O = dead space

A = analytical measurement

Q = quantity measurement

The maximum error for a calculated mixture adsorption value is shown in equation (G-7).

$$\text{Maximum Error for N} = \frac{\sum_{i=1}^{\gamma} Y_i N_i (1 + \gamma_A)(1 + \gamma_Q) - Y_O N_O (1 - \gamma_A)(1 - \gamma_Q)}{\sum_{i=1}^{\gamma} (Y_i N_i) - Y_O N_O} \qquad \text{(G-7)}$$

The probable errors for various points and conditions were calculated using equation (G-6). The same calculation was made by applying the variations directly to the data. These specific point computations agreed very well with the general relationship. As a result of these calculations, the conclusion was reached that the general precision for the carbon dioxide values in the mixture isotherms is ± 6% and the corresponding precision for the methane values is ±8%. The experiments which were repeated at various mixture points support these conclusions. Further, error bars of the size indicated allowed smooth lines to be drawn through the data points for each of the mixture isotherms.

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VITA

Kenneth Alfred Rogers was born April 9, 1927, in Chicago, Illinois to Grace Marie Draper and the late Alfred Clarence Rogers. He graduated from Lane Technical High School in 1945. He served in the U.S. Army from 1945 to 1947 which included one year with the paratroop infantry in Japan. He attended Northwestern University in Evanston, Illinois from 1948 to 1951 where he received the Bachelor of Science degree in Chemical Engineering. Upon graduation, he worked as a Design Engineer for Standard Oil of Indiana in Whiting, Indiana and left this position to work for Arabian American Oil Company in New York City as a Process Engineer in 1956. While there, he attended graduate school at New York University and Columbia University. In 1957 he returned to Chicago to work for Liquid Carbonic Corporation. After achieving the position of Chief Process Engineer, he left Liquid Carbonic in 1967 to take the position of Chief Engineer for W. F. H. Schultz Company in Doraville, Georgia. In 1968, he enrolled as a graduate student in the School of Chemical Engineering of the Georgia Institute of Technology. He received the Master of Science degree in Chemical Engineering in 1969. He was employed as an engineering consultant in the fields of process and equipment design since 1968. He taught in the School of Chemical Engineering during the 1971-72 school year. He is a member of Tau Beta Pi, Pi Mu Epsilon, and the Society of Sigma Xi.